APR 9 1924

Volume 8 Number 4

# Journal of the Optical Society of America and Review of Scientific Instruments

EDITOR-IN-CHIEF: PAUL D. FOOTE
BUREAU OF STANDARDS, WASHINGTON, D. C.
ASSISTANT EDITOR-IN-CHIEF AND BUSINESS MANAGER: F. K. RICHTMYER
CORNELL UNIVERSITY, ITHACA, N. Y.
CONSULTING BUSINESS MANAGER, M. E. LEEDS, PHILADELPHIA, PA.

Associate Editors:

| Term Ending Dec. 31, 1929 | Term Ending Dec. 31, 1927 | Term Ending Dec. 31, 1925 |
|---|---|---|
| E. C. CRITTENDEN | H. D. CURTIS | G. K. BURGESS |
| HERBERT E. IVES | WILLIAM DUANE | K. T. COMPTON |
| R. A. MILLIKAN | PAUL R. KLOPSTEG | L. R. INGERSOLL |
| L. P. SIEG | L. SILBERSTEIN | C. E. K. MEES |
| J. P. C. SOUTHALL | L. T. TROLAND | C. E. MENDENHALL |
| H. S. UHLER | F. E. WRIGHT | D. C. MILLER |

## APRIL, 1924

A Measurement of the Polarization of Secondary X-Rays ..... 487
ARTHUR H. COMPTON and C. F. HAGENOW

Magnetic Rotation in Sputtered Cobalt Films ..... 493
L. R. INGERSOLL

On the Active Agents in Luminescent Fluorspars and in Corundum and Spinel ..... 501
T. TANAKA

INSTRUMENT SECTION

The Measurement of Transmission in Instruments ..... 511
G. W. MOFFITT and PAUL B. TAYLOR

Calorimetry of Saturated Fluids ..... 519
NATHAN S. OSBORNE

A Photometric Disk Variable and Directly Readable while in Rotation ..... 541
ENOCH KARRER

A Source of Constant Frequency Oscillations ..... 545
ROSS GUNN

A Silver Chloride Battery for Potential Purposes ..... 549
HENRY A. ERIKSON

The Variation with Temperature of the Photoelectric Effect in Potassium Photoelectric Cells .. 551
HERBERT E. IVES

Reviews ..... 547, 548
Notes ..... 492, 543, 544, 580
Index to Advertisers ..... XXVII

Published Monthly by the
OPTICAL SOCIETY OF AMERICA

OFFICE OF PUBLICATION:
GEORGE BANTA PUBLISHING COMPANY
450-454 Ahnaip St.,
MENASHA, WISCONSIN

Entered as second-class matter May 31, 1921 at the postoffice at Menasha, Wis., under the act of March 3, 1879

# Journal
## of the
# Optical Society of America
## and
# Review of Scientific Instruments

Published monthly beginning May 1922.
Annual Subscription $5.00


The JOURNAL of the Optical Society of America was first published in January 1917. Four separate issues appeared in 1917, and two issues in 1919. During the years 1920 (Vol. IV) and 1921 (Vol. V) the JOURNAL was published bi-monthly. Copies of back numbers may be secured from the Business Manager for $1.00 each. The total charge for all numbers from Vol. I to Vol. V, 1921 inclusive, is $16.00. Only a small stock of the earlier issues remains. The six numbers comprising Vols. I to III will not be sold except in complete sets with Vols. IV and V.

By cooperation with the Association of Scientific Apparatus Makers of the United States of America the scope of the JOURNAL was enlarged beginning January 1922. As indicated by the present title the JOURNAL now publishes original papers on instruments of every description as well as papers on experimental and applied optics. The new JOURNAL is published monthly beginning May 1922, making 10 issues for 1922.

Annual Subscription $5.00 dating from January of the current year. Single copies $0.60. Remittances for subscriptions and back numbers should be made to "F. K. Richtmyer, Manager," Cornell University, Ithaca, N. Y.

All correspondence on the following subjects must be made with the Business Manager: (1) Application for, and checks in payment of annual subscriptions other than those of members of the Optical Society; (2) Change in mailing address; (3) Missing numbers: these will be replaced free of charge only when notification is made within 30 days from date of the immediately succeeding issue; (4) All advertising accounts and applications for space and rates.


THE OPTICAL SOCIETY OF AMERICA

*President*—HERBERT E. IVES,
Western Electric Co.,
New York, N. Y.

*Vice-President*—W. E. FORSYTHE,
Nela Research Laboratories,
Cleveland, Ohio.

*Secretary*—IRWIN G. PRIEST,
Bureau of Standards,
Washington, D. C.

*Treasurer*—ADOLPH LOMB,
Rochester, New York.

The Council consists of the above officers, the Editor-in-Chief and the Assistant Editor-in-Chief and Business Manager of the JOURNAL, the past President, L. T. Troland, Harvard University, and the following elected members: P. G. Nutting, Schenectady; K. T. Compton, Princeton University; F. E. Wright, Geophysical Laboratory; Carl W. Keuffel, Keuffel and Esser Co.


The object of the Optical Society of America is to serve the interests of all who are engaged in any branch of optics from fundamental research to the manufacture of optical goods.

The Constitution provides that anyone who has contributed materially to the advancement of optics shall be eligible to regular membership in the Society with the privilege of voting and holding office. Any individual or corporation interested in optics is eligible to associate membership. Annual dues including subscription to the JOURNAL are five dollars for individual membership and fifty dollars for corporation membership. Further information may be obtained from the Secretary.

Journal
of the
Optical Society of America
and
Review of Scientific Instruments

Vol. 8 APRIL, 1924 Number 4

# A MEASUREMENT OF THE POLARIZATION OF SECONDARY X-RAYS*

By Arthur H. Compton and C. F. Hagenow

ABSTRACT

It was observed by Barkla that the intensity of X-rays scattered from the second radiator perpendicular to the theoretical plane of polarization was about 1/3 as great as the intensity of the radiation in the plane. Since then evidence has accumulated that secondary X-rays even from light elements are not of the same wave-length as the primary rays. If this difference in wave-length is due to fluorescent radiation, it should result in an incomplete polarization of the scattered rays. The object of this experiment was to test this point by measurement of the degree of polarization of the scattered rays.

Heterogeneous X-rays of an average wave-length of about 0.25 A were scattered by paper, aluminium and sulphur. A geometric correction was made for the lack of complete polarization due to the solid angles subtended by the radiators, and the results were extrapolated to zero thickness of the radiators. The experiments indicate that, within a probable error of 1 or 2 per cent, the radiation is completely polarized. This precludes the possibility of there being any considerable amount of fluorescent radiation emitted from the radiator.

In his classic work on the polarization of scattered X-rays, Barkla observed that the intensity of the rays scattered from the second radiator perpendicular to the theoretical plane of polarization was about one third as great as the intensity of the radiation in the plane.[1] Had the polarization been complete, he should have observed zero intensity perpendicular to the plane of polarization. This result has been confirmed by later experimenters.[2] Barkla attributed this observed lack of complete polarization as due chiefly to the large cross section of the beams employed, so that most of the radiation was not scattered at exactly 90°. The evidence has recently become convincing that the secondary X-rays radiated even from light elements such as

* Based on a paper read before the American Physical Society, April 22, 1921.

[1] C. G. Barkla, Proc. Roy. Soc. 77, p. 247; 1906.

[2] e.g. Haga, Ann. d. Phys. *23*, p. 439; 1907.

carbon are not of the same wave-length as the primary rays,[3] a result inconsistent with the classical theory of scattering. While this difference may be explained by a quantum theory of scattering,[4] it has also been given the alternative interpretation that a large part of the secondary X-radiation is fluorescent rather than scattered.[5] If this fluorescent radiation is similar to the fluorescent $K$ and $L$ radiations, we should not expect it to be polarized, and a considerable lack of polarization of the secondary beam should result. If, on the other hand, the secondary beam is completely polarized at 90° with the primary beam, the hypothesis of fluorescence becomes difficult to defend. The present measurements of the degree of polarization of the secondary X-rays were undertaken primarily to test this point.

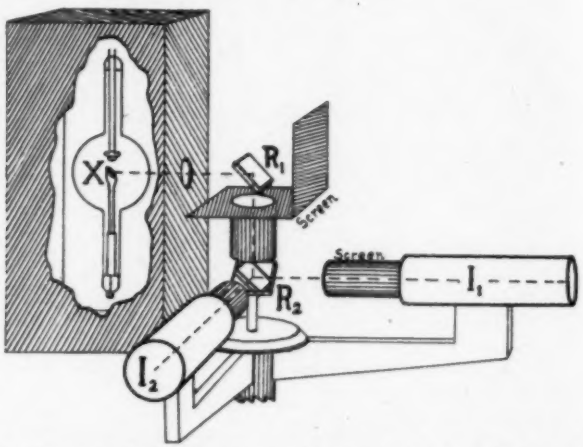


FIG. 1. *For completely polarized X-rays the intensity with the ionization chamber at $I_2$ should be very small compared with the intensity observed at $I_1$.*

The arrangement of the apparatus used is shown in Fig. 1. X-rays from the tungsten target $X$ of a Coolidge tube were scattered downward at right angles with the primary beam by the radiator $R_1$ to the radiator $R_2$. The radiator $R_2$ was placed upon the crystal table of a Bragg spectrometer, and scattered the rays into the ionization chamber. According to the usual theory, the intensity when the chamber was

[3] A. H. Compton, Bulletin Nat. Res. Council, No. 20, p. 16; 1922; P. A. Ross, Proc. Nat. Acad. Sci.; July, 1923.

[4] A. H. Compton, Phys. Rev. *21*, p. 483; 1923.

[5] e.g. J. A. Crowther, Phil. Mag. *42*, p. 719; 1921; A. H. Compton, Phil. Mag. *41*, p. 749; 1921.

placed at $I_2$ should be very small compared with the intensity with the chamber at $I_1$. The X-ray tube was operated at about 130 kilovolts peak and at a maximum of about 10 milliamperes, no absorbing screen being used. The effective wave-length was therefore about 0.25 A. The chamber was filled with methyl iodide, and the ionization current was measured with an electrometer whose sensitiveness was about 2000 divisions per volt. Under these conditions the deflections were conveniently large except when thin radiators were used.

On the basis of the usual view of scattering, there are two chief reasons for a lack of complete polarization when apparatus of this character is employed. The first is the fact that, since in order to obtain sufficient energy the radiators must subtend appreciable solid angles, not all the scattered rays which are used proceed at exactly right angles with the primary beam. The second is that an appreciable portion of the X-rays is scattered two or more times before leaving the radiator, and is hence incompletely polarized. This effect is especially pronounced when the radiator consists of a thick block.

An approximate calculation of the lack of polarization due to the solid angle subtended by the radiators can be made from the dimensions of the apparatus employed. The result of such a calculation of the ratio $R_G$ of the intensity at the position $I_2$ to that at $I_1$ is given by the expression

$$R_G = a^2\left\{\frac{.16}{k^2} - \frac{.52}{kl} + \frac{1.72}{l^2} - \frac{.52}{lm} + \frac{.16}{m^2}\right\}, \qquad (1)$$

where $k$ is the distance from the target to the radiator $R_1$, $l$ is the distance from $R_1$ to $R_2$, and $m$ is the distance from $R_2$ to the window of the ionization chamber. In deriving this expression, the radiators are supposed to consist of thin, square plates of edge $2a$, mounted at 45° as shown in Fig. 1, and the radiator $R_2$ is imagined to turn so that its upper face is always towards the ionization chamber. The effect of the solid angle subtended by the focal spot of the X-ray tube and by the window of the ionization chamber was neglected, since auxiliary calculation showed that the error from these sources was not appreciable.

In our experiments the dimensions were approximately, $k = 34$ cm, $l = 11.9$ cm, $m = 15$ cm, and $a = 2.5$ cm. Thus from equation (1) we find $R_G = 5$ per cent. Radiation of this intensity should therefore appear at $I_2$, even though the radiation scattered at 90° is completely polarized, and though no compound scattering occurs. We shall call this the *geometric correction*.

The error due to compound scattering is difficult to estimate quantitatively from the geometry of the problem. It can however be allowed for by using radiators of different thicknesses, and extrapolating the result to zero thickness. For small thicknesses, the ratio of the energy twice scattered to that scattered once is proportional to the thickness of the radiator. For somewhat greater thicknesses, the relative amount of energy scattered twice is approximately proportional to $se^{-bs}$, where $s$ is the mass per unit area of the plate, and $b$ is a constant depending upon the absorption coefficient of the rays in the plate. If $R_0$ is the ratio of the intensity at $I_2$ to that at $I_1$ for infinitesimal thickness of the radiators, the ratio for any surface density $s$ should be given approximately by the expression,

$$R = R_0 + ase^{-bs}. \tag{2}$$

The constants $R_0$, $a$ and $b$ can be determined from the experimental data. If the polarization is complete for rays scattered at exactly 90 degrees, the experimental value of $R_0$ thus determined should be identical with the value of $R_G$ calculated from equation (1). Since the form of equation (2) becomes more nearly exact as the surface density $s$ becomes smaller, it serves as a satisfactory formula for extrapolation to zero surface density.

The results of our experiments are shown in table 1, which gives the ratio $R = I_2/I_1$ of the intensities for different thicknesses and surface densities of the various radiators. Most of the figures are the averages of several series of readings. In taking the readings, the intensity was determined by taking the difference between the rate of deflection of the electrometer when both radiators were in place and the rate when radiator $R_2$ was removed. We thus avoided errors due to stray X-rays.

TABLE 1. *Polarization for Radiators of Different Thicknesses*

| Paper | | | Aluminium | | | Sulphur | | |
|---|---|---|---|---|---|---|---|---|
| Thickness, $t$ in cm | Surface density, $s$ in g/cm² | $I_2/I_1$, $R$ in o/o | $t$ | $s$ | $R$ | $t$ | $s$ | $R$ |
| .25 | .25 | 7 | .2 | .5 | 7 | .16 | .3 | 7 |
| .5 | .5 | 9 | .4 | 1.1 | 10 | .25 | .5 | 9 |
| 1.0 | 1.0 | 12 | .8 | 2.1 | 16 | .5 | 1.0 | 14 |
| 2.0 | 2.0 | 13 | | | | 1.0 | 2. | 13 |
| 4.0 | 4.0 | 18 | | | | 2.0 | 4. | 16 |

The effect due to the compound scattering for the greater thicknesses shows up very prominently in Fig. 2, in which are plotted the experi-

mental values of $R$ for different surface densities $s$ of the radiators. We find the most satisfactory agreement between equation (2) and the experiments if we choose $R_0 = 4.8$ per cent, $a = 8.4$, and $b = 2.57$. The agreement between the experimental value of $R_0 = 4.8$ and the calculated value of $R_G = 5$ per cent is thus very close. We feel justified in concluding from these experiments, therefore, that if the X-rays were scattered at exactly 90 degrees, and if both radiators were of infinitesi-

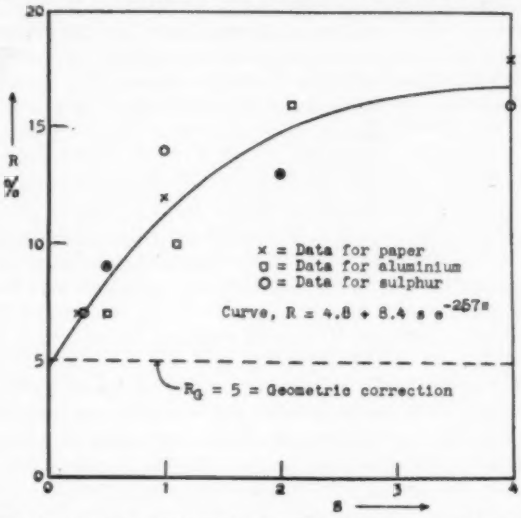


FIG. 2. *The fact that the experimental curve approaches the geometric correction for thin radiators indicates that within experimental error the rays scattered at 90 degrees are completely polarized.*

mal thickness, the intensity of the rays entering the ionization chamber at $I_2$ would probably be not more than 1 or 2 per cent as great as with the ionization chamber at $I_1$.

The almost perfect polarization which this result implies leaves no room for any considerable amount of fluorescent radiation in the secondary rays similar to the characteristic fluorescent radiatione observed with the heavier elements.[6] Our experiments are on the other hand in complete accord with the view that all the rays from these light elements are truly scattered.

A. H. C., UNIVERSITY OF CHICAGO,
CHICAGO, ILLINOIS.
C. F. H., WASHINGTON UNIVERSITY, SAINT LOUIS, MISSOURI.

[6] Note added March 4th: It is inconsistent also with the existence in our experiments of any appreciable "tertiary" x-radiation, of the type suggested by Clark, Duane and Stifler to account for the increased wave-length of the secondary radiation.

**Critical Electron Energies in Hydrogen.**—By means of a tube abounding in grids and filaments, Horton and Miss Davies identify the critical potentials of (*a*) inelastic impacts, (*b*) excitation of radiation, and (*c*) ionization, in hydrogen; and further (*d*) are able to discriminate between radiations from the atom and radiations from the undisrupted molecule. Inelastic impacts, recognized by sudden dips in the curves representing electron currents which overcome a small constant retarding voltage after being accelerated by a large variable one, occur at 11.9, 15.9, and 22.8 volt. Radiation potentials are located by sudden bends in the curves representing current into the collecting electrode, the bends being in the sense indicating an outrush of electrons excited from the metal by the radiation; ionization potentials by sudden bends in the contrary direction; none of the primary electrons is allowed to reach the collector. Radiation potentials were found at *10.2*, 11.9, 12.6 and 26.1; ionization potentials at 10.5, *13.6*, 15.9 and 29.4. The italicized ones are manifested by such feeble bends that the authors ascribe them to *H*, in accordance with Bohr's values. On the other hand, a photoelectric effect is produced on a gauze entirely screened from the scene of impacts, when the voltage passes 12; indicating that the radiation emitted at 11.9 is emitted by molecules and passed along through the gas from molecule to molecule by successive absorptions and re-emissions (whereas if it were emitted by atoms it would find practically no atoms free in the gas to transfer it along). This experiment is performed with the impacts occurring in one arm of an *H*-shaped tube and the gauze in another arm; the authors convinced themselves that no perceptible amount of radiation can find its way from one arm into the other by reflection from walls. Of the remaining three ionization potentials, the one at 10.5 is believed to be spurious; while at 15.9 dissociation of the molecule and the ionization of one atom occurs, and at 29.4 (15.9+13.5) dissociation and ionization of both atoms. The remaining two radiation potentials can be interpreted as dissociation plus excitation of one atom, without or with ionization of the other. These interpretations, however, require that 2.4 volts be taken as the work of dissociation of $H_2$. The inelastic impacts at 22.8 volts may ionize the molecule without dissociating it. Some uncertainty is introduced into the numerical values by the initial velocities of the thermionic electrons, the correction for which is determined by cutting down the electron stream by an adverse voltage applied just in front of the filament, and increased until the bend in the curve revealing the critical potential is on the verge of vanishing. Curiously enough this method yields different corrections for different critical potentials, altering thus the directly observed differences between them as well as their absolute values. Study of the spectrum of the hydrogen indicated that Balmer series and secondary spectrum lines alike occur from 15.9 volts upward, and that a blue glow with a continuous spectrum extending as far as the red appears at or about 12.6 volts.—[F. Horton and A. C. Davies; Phil. Mag. *46*, pp. 872-896; 1923.] K. K. DARROW

# MAGNETIC ROTATION IN SPUTTERED COBALT FILMS

By L. R. Ingersoll

ABSTRACT

**The effect of heat treatment on magnetic rotation in sputtered cobalt films.** The films were prepared in a *special depositing chamber*, the main feature of which was an arrangement for keeping the films cool during the process of sputtering.

Magnetic rotation measurements were made over the wavelength range .6$\mu$ to 2.3$\mu$ on such cathodically sputtered cobalt films before and after heating for a number of hours at about 300°C in low pressure palladium-pure hydrogen. The result of this heat treatment was to increase several-fold the rotations at 2$\mu$ for both the Faraday (transmission) and Kerr (reflection) effects, while towards the visible the change was small.

Conclusions drawn from this are based on the assumption that heat treatment coalesces the granules of which the film is composed into larger units. Then since the magnetic rotation is seen to depend on the size and character of the particles, it should be regarded in this case as a *molar* rather than molecular or atomic property, the effects being determined by conducting electrons even for wavelengths as short as 1$\mu$.

*Experiments on a nickel film and on colloidal iron* yielded results in agreement with this conclusion.

Magnetic rotation of the plane of polarization of transmitted (or reflected) light has been studied for thin films of the ferromagnetic metals, produced in various ways, by a number of investigators.[1] So far as the writer is aware, however, these films have been tested in the same general condition as when produced, without any systematic attempt at studying the effect of heat treatment.

Now during the last few years there has been considerable investigation of the resistance of cathodically deposited metal films, particularly as regards the effect of heating or other means of artificial ageing. In general the resistance of a sputtered film decreases with time, a process which is accelerated by vacuum- or heat-treatment. The work of Richtmyer[2] and others indicates clearly that this ageing is really a coalescing of the granules which compose such a film into particles (probably crystals in most cases) of larger size, and this explains the change of resistance. The effect is so marked that it seemed to the writer that it would be particularly interesting to investigate in this connection another property, likewise electronic in character, that is, magneto-optic rotation.

[1] Vide L. R. Ingersoll, Phil. Mag. (6) *18*, p. 74; 1909, for references.

[2] F. K. Richtmyer and L. F. Curtis, Phys. Rev. *15*, p. 465; 1920, L. F. Curtis, Phys. Rev. *18*, p. 255; 1921, L. R. Koller, Phys. Rev. *18*, p. 221; 1921, and others.

## PREPARATION OF FILMS

Previous experience[3] with cathode films of the ferromagnetic metals having shown that the least trace of air or water vapor produces a

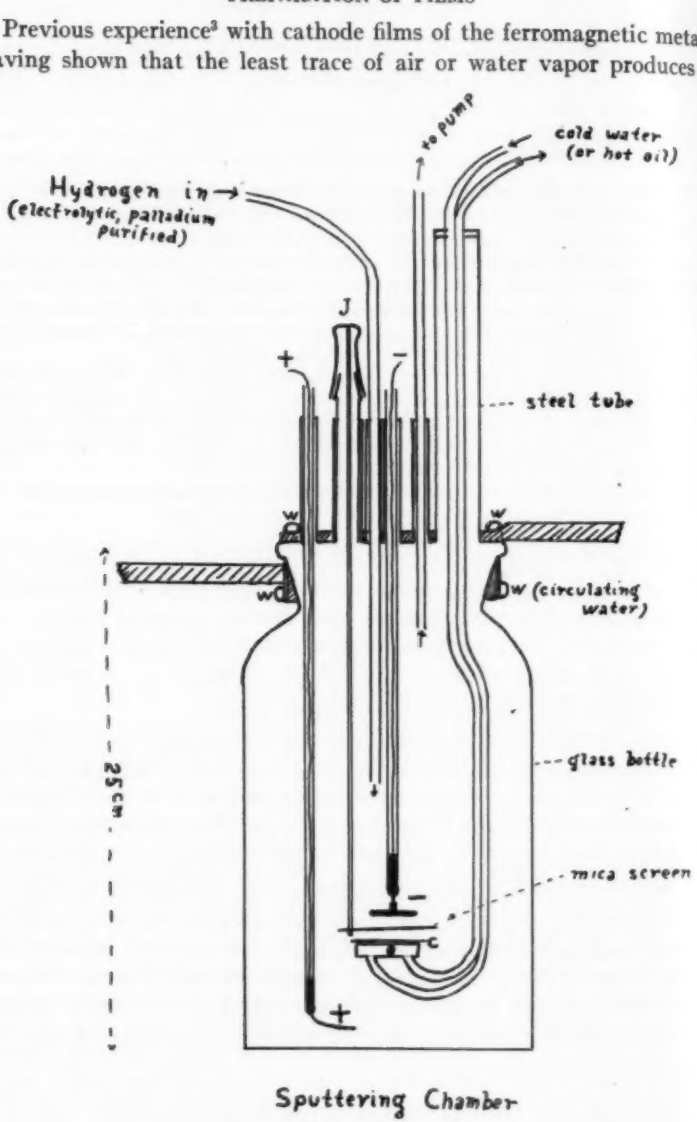


FIG. 1

[3] Phil. Mag. *loc. cit.*

disastrous oxidation during deposition, a special chamber was designed which allowed of preliminary baking and also accomplished certain other purposes. This is shown in Fig. 1. All the entries were made through a brass top plate, clamped independently of the glass vessel, which was an ordinary wide-mouthed candy jar. The joint was sealed with "half-and-half" wax, whose use in this case was allowable since a continua stream of hydrogen under pressure of a tenth of a millimeter or so was flowing through the chamber while deposition was going on. The hydrogen was electrolytically generated, dried and then passed through a heated palladium tube as final assurance of its purity. Other precautions against oxidation were preliminary baking—the collar and brass plate were water-cooled to permit this—and a final out-gassing by passing the discharge for half an hour before the mica shield was turned aside and the film deposition begun. The current was furnished by a 1200 volt D. C. dynamo set and averaged about 20 m. a.

*The chief novelty in design*, however, was the small copper box or film holder (the outgrowth of a suggestion by Professor Richtmyer) by which the temperature of the film could be controlled during deposition by circulating hot oil, cold water, or, for that matter, liquid air. To avoid thermal complications the copper tubes entered through a 15 cm length of steel tube, all the joints being brazed.

From the writer's viewpoint the most interesting results were to be expected from films deposited on a chilled (water-cooled) surface and these have been the only ones produced so far. Some of the films tested were, in fact, made in a somewhat simpler depositing chamber but under conditions which kept them relatively cool during the sputtering. The best films were of a clear gray color, slightly bluish.

After deposition the microscope cover glass bearing the film was cut into half a dozen pieces each about 5 mm $\times$ 25 mm. The magnetic rotation dispersion of one of these strips was then measured, after which it was baked in a glass tube in low pressure hydrogen for some hours at a temperature in the neighborhood of 300° C and then its rotation tested again. When not in use all films were kept in a desiccator.

With the exception of one or two experiments on nickel the only metal tested so far in this way has been cobalt. The cathode was sawed from a piece which had been formed by melting a very pure "nickel-free" cobalt in finely divided state. Magnetic rotation was measured by the bolometric method[4] over a spectral region embraced between the wavelength limits .6$\mu$ and 2.3$\mu$. Correction was made for the small

[4] Vide L. R. Ingersoll, Phil. Mag. loc. cit., Jour. Opt. Soc. Am. *5*, p. 156; 1921.

rotation due to the microscope cover glass on which the film was deposited. The rotations plotted are the (double) ones due to reversal of the magnet current, for films averaging 50$\mu\mu$ in thickness, in a field of about 10 kilogauss.

## RESULTS

Fig. 2 shows the general form of the rotation dispersion curve before and after heat treatment. The chief characteristics are the small

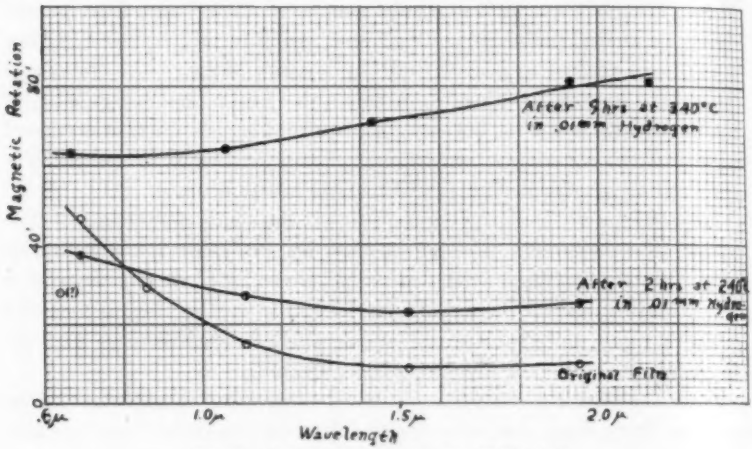


FIG. 2. *Faraday rotation for film 106E-cobalt.*

change in rotation produced by ageing at the visible end of the spectral region studied, and the large change—in some cases ten-fold—in the infra-red.

Fig. 3 shows the results of prolonged heat treatment, and we might gather from this that the effect produced by a temperature of 300°C. is practically complete at the end of a dozen hours or so. Fig. 4 shows the progressive effect of several short treatments.

In one case the (polar) Kerr effect or rotation on *reflection* was measured (Fig. 5) and it will be noted that the curve exhibits the same general characteristics of small change for shorter wavelengths and large for longer.

*Interpretation of the Curves.* One of the first points of interest brought out by the curves is this:—The similarity of the results of heat treatment for the Faraday, or transmission, and Kerr, or reflection rotation indicates that both these effects must be controlled by the same general

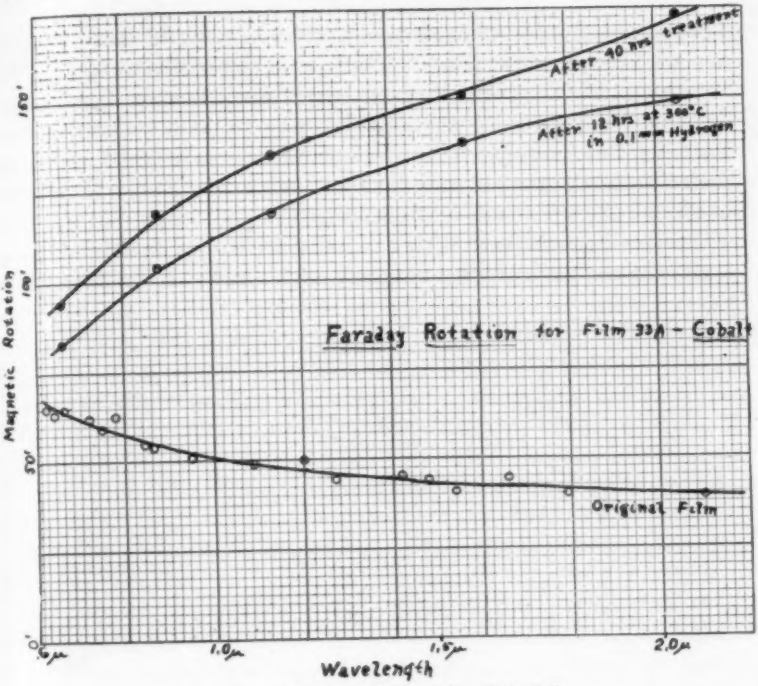


FIG. 3. *Faraday rotation for film 33A-cobalt.*

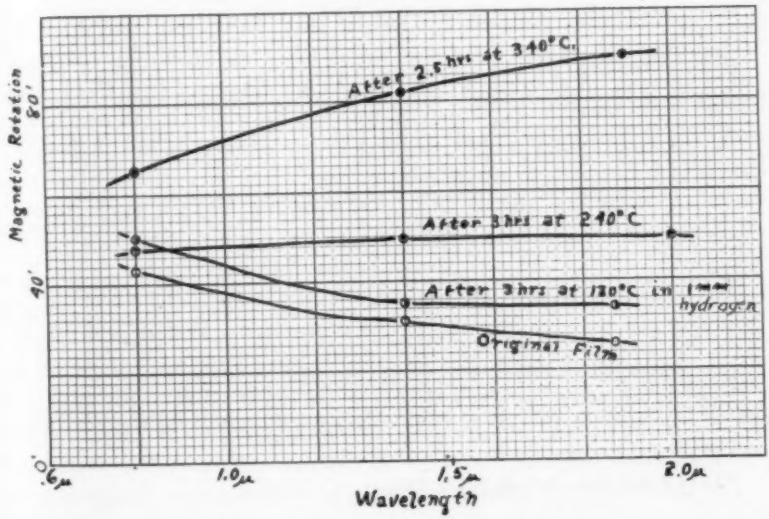


FIG. 4. *Faraday rotation for film 37B-cobalt.*

mechanism. Our theories for these phenomena, as they stand at present, are not very satisfactory. There are several different ones for the Faraday rotation and while we need perhaps consider only that of Voigt for the Kerr, it is rather complicated. The close connection indicated by the foregoing results can hardly be overlooked in future theoretical development along this line, and for the remainder of this article the two effects will be classed together.

Perhaps the most interesting conclusion which can be drawn from a study of these curves is that magneto-optic rotation in such films is—

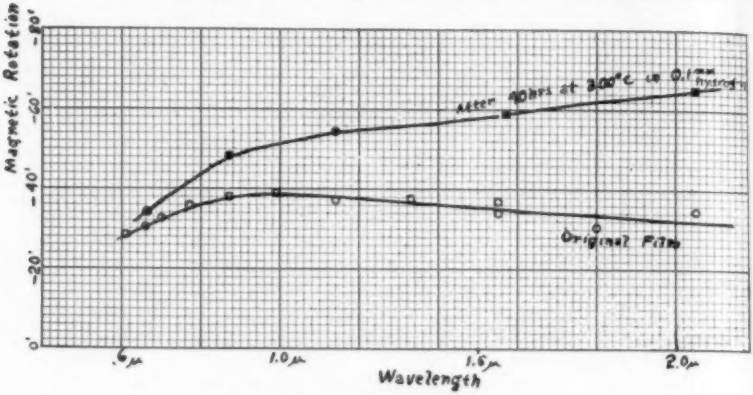


FIG. 5. *Kerr rotation for film 33A-cobalt.*

since it obviously depends on the size and character of the granules composing the surface—a *molar* rather than an *atomic* or *molecular* phenomenon. A number of years ago Voigt[5] discussed in a theoretical paper some previous experimental work of the writer's and concluded that the Kerr magneto-optic rotation at wavelength $2\mu$ in cobalt (and steel) is due mainly to *conducting electrons*. The present results would seem to strengthen greatly this conclusion and make it apply to the Faraday rotation as well. Furthermore we can now push this wavelength down to $1\mu$ and even almost to the visible spectrum.

*An Optical Analogy.* There is an analogy in another field of optics which is not without interest in this connection. Wente[6] and others have shown that for short electromagnetic or long infra-red radiation a surface consisting of very short metal strips, or "linear resonators," has a much lower reflecting power than a continuous one. When the

[5] Phys. Zeit. *16*, p. 299; 1915.
[6] E. C. Wente, Phys. Rev. *16*, p. 133; 1920.

strips increase in size to about one-tenth of the wavelength the reflecting power begins to go up and in fact reaches a maximum (Wente's experiments) when they are about one-third wavelength long.

That some such action—barring, perhaps, the resonance effect—is taking place here seems certain. However, a quantitative connection between the magnitude of the rotation, either on transmission or reflection, and the size of the granules seems difficult to establish, not only because of the great variety of sizes, but also on account of the difficulty of measuring them. While some observers have been able to see with a microscope the granular structure in sputtered films of certain metals, no evidence of granulation could be detected in these cobalt films even with oil-immersion objective, with the exception of a very old film which gave some indication. Under the ultra-microscope, however, the granular structure was clearly indicated with, as might be expected, a large variety of sizes. But since the ultra-microscope requires thinner films than are useful for magneto-optic measurements, it is not entirely certain that the granular structure in these thin films can be taken as identical with that of the thicker ones. This matter, however, is to be investigated further.

This much is true, however: the films after treatment showed a somewhat higher reflecting power (casual inspection) and much smaller transmission (actual measurement) than before. The change in transmission, however, was relatively independent of the wavelength, which fact points away from any direct quantitative relationship between this phenomenon and magnetic rotation.

*Other Experiments.* Two other experiments should be mentioned in this connection. Colloidal iron in isobutyl alcohol showed no detectable rotation above that of the alcohol itself, although the particles of iron were so magnetic that they were soon swept by the field onto the glass. Also a sputtered film of nickel showed no rotation until subjected to heat treatment, when its magneto-optical property became very apparent. The suggested explanation is that in each case—the colloidal iron and untreated nickel film—the particles were too small to show the effect for the wavelengths used (about .7$\mu$ to 1.6$\mu$).

*Other Possible Explanations.* There are one or two alternative explanations which might be urged in place of the foregoing, which may be briefly considered. The first is on the basis of the Weiss internal magnetic field which undoubtedly plays an important part in magnetic rotation in ferromagnetic metals. It is entirely possible that this and other magnetic characteristics of the film change on heat treatment

although it would probably be hard to prove experimentally. It seems reasonable to expect, however, that such a field change would affect all wavelengths equally, and this is not in agreement with experiment.

The other matter is not so easily disposed of. In a study of the crystalline structure of a number of common metals Hull[7] finds that while cobalt seems to occur ordinarily in a hexagonal, close-packed lattice form, it may be at least partially changed to the face-centered cubic by prolonged heating in hydrogen at 600°C. That there would be some tendency for the films to undergo this change in the present case cannot be disputed. The temperatures, however, are much lower than that specified by Hull, while variation in hydrogen pressure in heat treatment from a centimeter down to a hundredth of a millimeter or so did not affect the results appreciably.[8] The exact crystalline structure of the films remains to be investigated. Preliminary tests have failed, indicating the need for much thicker films, and while there may be some question as to such films having the same structure as the thinner ones it is believed that some check can be had on this through measurements on the Kerr effect.

In conclusion, I wish to acknowledge my indebtedness to both the Rumford and American Association funds for former grants which have aided this research. I wish also to express my appreciation of the assistance of Mr. Elmer O. Kraemer in some of the chemical matters, while I am particularly indebted to Mr. S. S. DeVinney for his assistance, both in depositing films and making rotation measurements.

PHYSICAL LABORATORY,
UNIVERSITY OF WISCONSIN,
DECEMBER 11, 1923.

[7] A. W. Hull, Phys. Rev. *17*, p. 577; 1921.

[8] It may be remarked that this apparent independence of hydrogen pressure would seem to exclude any explanation of the phenomena purely on the basis of absorbed gas.

# ON THE ACTIVE AGENTS IN LUMINESCENT FLUORSPARS AND IN CORUNDUM AND SPINEL

By T. Tanaka

This paper describes further researches in identifying the active agents of luminescent substances, continuing the work on luminescent calcites, aragonites and dolomites.[1] Studies of the following substances are here discussed: 17 samples of fluorspar. 2 samples of corundum. 1 sample of artificial ruby. 1 sample of spinel. Most of these samples were furnished by the department of mineralogy of Cornell University through the kindness of Professor Gill, to whom the author is especially indebted.

## Fluorspars

Fluorspars are often found in a quite pure state; and there is no one impurity almost inevitably present in them, such as manganese in the calcites, and chromium in alumina. Very careful chemical or spectral analyses often fail to detect the presence of any trace of manganese in luminescent fluorspars. Nevertheless some authors attribute the continuous luminescence in the green region, which occurs in some samples, to that metal. Magnesium, aluminium, iron, sodium, etc. may occur as impurities in fluorspars, but their luminescent power is too low for them to be considered as the chief active agents. Therefore, the active agent must be some element having a high luminescent power, and which is contained in so minute a quantity that it escapes detection by ordinary analyses — probably some rare earth metal.

The wide distribution of yttrium in minerals has been repeatedly mentioned by Crookes, while Humphreys[2] by spectral analyses found that of 129 samples of fluorspar examined by him, 117 contained yttrium and 27 ytterbium. Morse[3] who examined the fluorescence spectra of some samples of fluorspar tried in vain to find any systematic occurrence of the bands when the samples were excited by different kinds of electric spark. Next he studied the thermoluminescence spectra of two samples of chlorophane[4] (a strongly thermoluminescent variety of fluorspar) and found that they coincided. He tried to find some relation between these spectra and that supposed by Crookes to be due

[1] Tanaka; J.O.S.A. & R.S.I. *8*, p. 411, 1924.
[2] Humphreys, W. J.; Astrophys. Jour. *20*, pp. 266-273; 1904, and *22*, p. 159, 1905.
[3] Morse, H. W.; Astrophys. Jour *21*, pp. 85-100; 1905.
[4] Morse, H. W.; Astrophys. Jour. *21*, pp. 410-417; 1905.

to yttrium, but without success. Urbain[5] studied the solid solutions of many rare earths and determined their characteristic bands. Comparing these with the spectra of some samples of fluorspar, he arrived at the following conclusions: (1) Two samples of fluorspar showing green luminescence have ytterbium as the active agent; one sample showing red luminescence has praseodymium as active agent; one sample showing rosy white luminescence has samarium and dysprosium as active agents. (2) The luminescence of a certain sample of chlorophane can be explained as the superposition of spectra due to samarium, ytterbium, dysprosium and gadolinium. The recognition of so many metals as chief agents of the luminescence of fluorspars is not unreasonable; it is an old saying that every element could be detected everywhere had we sufficiently delicate tests for it. At any rate the whole question must be said to have been left undecided.

Although in most samples of fluorspar the perceptible spectrum extends into the violet, bands in that region are not included in the following tables. As we approach the violet end of the spectrum, on account of the decreased sensibility of the eye, and the increased dispersion, observations are difficult; and, moreover, the crowding of the members of the series characteristic of different metals makes the identification of the origin of any band in this region very uncertain. The violet end of the spectrum is of little use therefore for the present purpose, and observations, made by the method used in the study of calcite[6] were restricted to other portions of the spectrum.

Throughout the tables, the wave lengths of the crests in the spectrum of the sample studied, are given in A. U., while discrepancies between these and the wave lengths of the crests in the spectrum of the metal with which they are identified are indicated by inverting in brackets the last digit in the wave length of the metallic band: e.g. 5793(2). This means that the band characteristic of the active metal is at 5792 while that in the spectrum of the fluorspar was read as 5793.

TABLE 1. *Fluorspars*

| Substance | Active Agents | Bands identified |
|---|---|---|
| Fluorspar I | Sa(14) | 5277(5), 5248(0), 5227(9), 5193, 5184(3), 5137, 5082(3) 5029(0), 5010, 4979(8), 4928(7), 4887, 4848, 4696. |
| | Yt(4) | 5386, 5317, 5151(9), 5089(1). |
| | La(3) | 4950, 4792(9), 4721. |

[5] Urbain; Ann. de Chim. et Phys. 8, *18*, p. 222; 1909.

[6] Tanaka; *loc. cit.*

TABLE 1—*Continued*

| Substance | Active Agents | Bands identified |
|---|---|---|
| Fluorspar II | Sa(18) | 5181(3), 5139, 5080(3), 5052, 5030, 5010, 4967(8), 4887, 4828, 4780, 4732(3), 4696, 4661(9), 4623, 4597, 4588, 4551(3), 4519. |
| Fluorspar III | Sa(17) | 5308, 5250, 5193, 5138(9), 5081(3), 5053(2), 5030, 5008(0), 4979(8), 4965(8), 4928(7), 4887, 4847(8), 4807(9), 4778(0), 4733, 4696. |
| | Ce(2) | 5159(8), 5114(2). |
| Fluorspar IV | Sa(17) | 5468, 5429(7), 5364(7), 5325(2), 5183, 5140(9), 5031(0), 5009(0), 4929(8), 4847(8), 4827(8), 4808(9), 4781(0), 4696, 4658(9), 4550(3), 4511. |
| | Yt(6) | 5399(7), 5270, 5090(1), 4767(6), 4715(6), 4619. |
| | La(2) | 4950, 4745. |
| Fluorspar V | Sa(23) | 5470(8), 5418, 5368(0), 5308, 5275, 5231(9), 5141(9), 5138(7), 5098(5), 5085(3), 5052, 5030, 5010, 4978, 4967(8), 4925(8), 4876(7), 4808(9), 4733, 4685(7), 4639(1), 4587(8), 4509(1). |
| | Mn(2) | 4919(1), 4541. |
| | Yt(2) | 4764(3), 4716. |
| Fluorspar VI | Sa(20) | 5307(8), 5274(5), 5082(3), 5052, 5030, 5014(0), 4978, 4928,Y 4890(7), 4851(8), 4831(8), 4809, 4780, 4731(3), 4639(1), 4597, 4553, 4509(1), 4485(8), 4426(8). |
| | La(3) | 5074(5), 4997(9), 4951(0). |
| | Yt(2) | 5149, 5115(8). |
| Fluorspar VII | Sa(17) | 5489, 5231(9), 5138(7), 5052, 5008(0), 4969(8), 4929(8) 4845(8), 4778(0), 4732(3), 4688(7), 4659, 4624(3), 4595(7), 4555(3), 4510(1), 4451. |
| | Ce(4) | 5205(4), 5168(9), 4898(7), 4814(6). |
| | Yt(2) | 5333, 4765(3). |
| | Yb?(1) | 5128(9). |
| Fluorspar VIII | Sa(23) | 5465(8), 5418, 5308, 5277(5), 5229, 5184(3), 5137, 5095, 5083, 5031(0), 4967(8), 4927, 4888(7), 4848, 4830(8), 4810(9) 4782(0), 4734(3), 4688(7), 4662(9), 4623, 4556(3), 4519. |
| | Yt(4) | 5209, 4992(4), 4716, 4605(3). |
| | Dy(1) | 4753(5). |
| | Ce(1) | 5348. |
| Fluorspar IX | Sa(13) | 5470(8), 5369(0), 5322, 5229, 5183, 5052, 5031(0), 4978, 4927, 4886(7), 4847(8), 4809, 4780. |
| | Dy(2) | 5410, 5109. |
| Fluorspar X | Sa(12) | 5420(8), 5373(0), 5308, 5250, 5192(3), 5083, 5032(0), 4976(8), 4828, 4782(0), 4655(9), 4623. |
| | Er(3) | 5151, 4943, 4898. |

## NOTES ON TABLE 1

FLUORSPAR I. (from Castleton, Derbyshire, England.) Color yellow, luminescence faint violet. Fourteen samarium, four yttrium, and three lanthanum bands were identified. The presence of small quantities of yttrium in some fluorspars from the same locality was proved by Humphreys, hence the appearance of a few yttrium bands is not surprising, though this can not be considered the chief active agent. Lanthanum belongs to the same group as samarium, so their bands might be expected to occur together. The occurrence and luminescent power of samarium will be discussed at the end of this section.

FLUORSPAR II. This sample was furnished by Vassar College. Color bluish green, luminescence a fairly bright violet. Eighteen samarium bands were found. Certain bands due to erbium seemed to occur in an indefinite way, and are not included in the table.

FLUORSPAR III. This sample, like the preceding, was furnished by Vassar College. Color light blue, luminescence a bright indigo. Seventeen samarium and two cerium bands were identified. The presence of cerium in fluorspars is well known.[7]

FLUORSPAR IV. (from Weardale, Durham, England). Color bright violet, luminescence also bright violet. Seventeen samarium, six yttrium and two lanthanum bands were identified; also one band due to an element which was probably ytterbium. Humphreys proved the presence of a fair amount of yttrium and a small amount of ytterbium in fluorspars from the same locality; but these are certainly far from being the chief agents of luminescence in this case.

FLUORSPAR V. (from near Rosiclare, Illinois). Color light blue. Luminescence blue of medium intensity. Twenty-three samarium, two manganese and two yttrium bands were identified. Humphreys found traces of yttrium in fluorspars from the same locality.

FLUORSPAR VI. (from Cumberland, England). Its color was purple. Luminescence blue of medium intensity. Twenty samarium, three lanthanum and two yttrium bands were identified. Humphreys found a fair amount of yttrium in fluorspars from this locality, but that metal does not seem to play an important part in the luminescence.

FLUORSPAR VII. (from New Hampshire). Color a beautiful grass-green, luminescence fairly bright and of a light violet color with a blue tint. Seventeen samarium, four cerium and two yttrium bands were identified, also one band due to an element which is supposed to be ytterbium. Humphreys found a fair amount of yttrium and traces of ytterbium in several grass-green samples of fluorspar from the same locality.

FLUORSPAR VIII. The origin of this and of the succeeding samples of fluorspar is unknown. This sample had a yellow natural color, and showed a fairly bright, light luminescence. Twenty-three samarium and four yttrium bands were identified; also one dysprosium band and one cerium band. The dysprosium band was very sharp and always occurred in every one of the repeated experiments; and the wavelength of its crest was quite different from any due to any other probable agent. Hence the presence of dysprosium may be recognized without any hesitation.

FLUORSPAR IX. Color a yellowish brown, luminescence a green of medium intensity. Thirteen samarium and two dysprosium bands were recognized. The high luminescent power of dysprosium dissolved in calcium fluoride was demonstrated in a previous paper.[8]

FLUORSPAR X. Color violet, luminescence a fairly bright violet. Twelve samarium and three erbium bands were identified. The high luminescent power of erbium was also established in the studies just cited.

FLUORSPAR XI. Color blue, luminescence a fairly bright purple. The spectrum consisted clearly of two groups of bands, one situated in the orange and the other in the blue. These were resolved into thirteen samarium, twelve thallium, and five yttrium bands, in the region between 5800 and 4600 A. U. To judge from relative intensity, thallium played rather a

[7] Loew, P. O.; Berichte der Deutschen Chem. Gesellschaft *14*, p. 1144; 1881.
[8] Tanaka, T.; *loc. cit.*

more important part in the luminescence than did samarium, in both portions of the spectrum. The general appearance, also, was similar to that of the spectrum of thallium dissolved in calcium fluoride, as previously studied by the author.

FLUORSPAR XII. Color light blue, luminescence a fairly bright violet. Twenty-one samarium and four thallium bands were identified in the region of 5625-4700 A. U. The spectrum consisted of two groups of bands, one being situated in the blue region and the other, quite faint, in the yellow. In this case thallium played no very important part in the phenomenon.

FLUORSPAR XIII. Color a beautiful green, luminescence a fairly bright violet. Twenty-four samarium, seven thallium and four praseodymium bands were identified in the region 5600-4600 A. U. The spectrum was very similar to that of Fluorspar XII. The chief active agent was samarium.

FLUORSPAR XIV. Color a light green, luminescence a fairly bright, light violet. Seventeen samarium and eleven thallium bands were identified, also two bands due to an element which is supposed to be ytterbium. The appearance of the spectrum was similar to those of Fluorspars XI and XII. The luminescence is to be attributed chiefly to samarium and thallium.

FLUORSPAR XV. Color a light blue, luminescence a violet of medium intensity. Fifteen samarium and nine praseodymium bands, also one thallium band were identified in the region of 5500-4700 A. U. The bands in the yellow region were all faint. Samarium was the chief active agent.

FLUORSPAR XVI. Colorless, luminescence a faint violet. Seventeen samarium, three yttrium and three gadolinium bands were identified in the region 5400-4600 A. U. The chief active agent was doubtless samarium.

FLUORSPAR XVII. White and opaque, luminescence a faint violet. Seventeen samarium, nine manganese and four cerium bands were identified in the region 5500-4600 A. U. The chief effect is to be attributed to samarium.

The wide distribution of traces of samarium and of yttrium was mentioned again and again by W. Crookes,[9] but the researches of Lecoq, Baur and Marc, etc., proved his reasoning in respect to yttrium to be totally wrong. He believed in the possibility of luminescence in pure rare earths, and observed in his "pure yttrium" a "citron-colored band" which he considered to be characteristic of that metal. He describes especially the spectrum shown by pure ignited yttric sulphate in a radiant matter tube as "one of the most beautiful objects in the whole range of spectroscopy," and states that that spectrum showed an intensely brilliant citron-colored band. These statements show very clearly that the origin of the "citron-colored band" can not be yttrium. But there is no fault in his reasoning with respect to samarium.[10] He recognized the impossibility of luminescence in pure samarium salts, and mentioned the remarkable sensibility and intensity of luminescence of the solid solutions of samarium. He observed the characteristic orange band in a solution consisting of 1 part of samarium to 1,000,000 parts of calcium.

Considering the wide distribution and high luminescent power of samarium, it is reasonable to attribute the chief effect in the samples of fluorspar so far studied to that element. There was, however, one seeming discrepancy. Calcium fluoride mixed with a small quantity of samarium was proved by Urbain and others[11] to emit a yellowish orange light, and this was the result obtained by the present author in his previous studies; while the luminescent colors of the samples of fluorspar observed in this investigation were violet blue, or green. To test the matter further several small pieces taken from the before-described samples of fluorspar were heated to red heat and then put into the cathode ray tube. It was surprising to see that almost all parts of the surfaces of the pieces emitted beautiful orange light, while a few small

[9] Crookes, W.; Chem. News, *49*, pp. 159-160, 169-171, 181-182, 194-196, 205-208; 1884.
[10] Crookes, W.; Chem. News, *51*, pp. 301-303; 1885.
[11] Urbain, M. G.; Ann. de Chim. et d. Phys. *8*, p. 18; 1909.

parts emitted violet, blue, or green lights of varying shades, perhaps because they had been insufficiently heated. This served as a reminder of the sample of calcium fluoride which had been proved to contain a small quantity of samarium, and which, without previous heating, showed a violet luminescence.[12] The effect of heating on the luminescent color of that sample was therefore investigated. After heating in an open crucible with the luminous flame from a Bunsen burner the luminescence became blue. After heating with a colorless flame from a Bunsen burner it became greenish blue. Lastly, after heating to red heat with a gas-blowpipe the luminescence turned a beautiful orange. The bands found in this case belonged to the same series of samarium as those previously observed for this sample. By adding a small quantity of samarium, the luminescent color at each stage of the heating increased perceptibly. After this, the same sample was kept in a closed glass tube for about six months, and was then tested again. It showed a green luminescence. Upon being heated to red heat the luminescence became once more orange.

Several cases are known in which the color of luminescence is entirely changed by changes in concentration and in the previous heat treatment of the substance.[13] Therefore in many cases the color of luminescence is not a good criterion by which to identify the active agent. The statement may hold good in the case of fluorspars. In the course of slow variations in the physical condition after previous heating, each sample may emit luminescent light of orange, green, blue or violet, even though violet may be the color corresponding to the most stable state of the substance.

### Summary of the Experiments on Fluorspars

(1) In most samples of fluorspar the chief active agent is samarium.

(2) Other active agents are yttrium, thallium, lanthanum, cerium, probably ytterbium, etc.

(3) The luminescent colors are violet, blue, and green but these may change to orange when the substance is heated.

### Corunda and Spinel

It has been long known[14] that alumina shows a beautiful crimson fluorescence under the action of light of high refrangibility, or of an electric discharge. Concerning the origin of this luminescence, many opinions have been advanced by both physicists and chemists. Among them, Lecoq[15] insisted from first to last that pure alumina is non-luminescent, and that its luminescence is due to the presence of a small quantity of some chromium salt. Becquerel[16] agreed that the addition of a small quantity of some chromium salt increased the red luminescence of alumina, but insisted that pure alumina itself becomes luminescent when heated to a sufficiently high temperature. He considered

[12] Tanaka, *loc. cit.*

[13] Becquerel, E.; Ann. Chim. et Phys. (3), *55*, pp. 5-119; 1859. A. Verneuil, C. R. *103*, pp. 600-603; 1886. E. Wiedemann und G. C. Schmidt, Ann. der Phys. und Chem. *56*, pp. 201-254; 1895.

[14] Becquerel, E.; Ann. de Chim. et Phys. (5), *57*, p. 125; 1859, and (5), *62*, p. 90; 1861.

[15] Lecoq de Boisbaudran, C. R. *103*, pp. 1107, 1224-1227 and *104*, pp. 330-334, 478-482, 554-556, 824-826; 1887.

[16] Becquerel, E.: Ann. de Chim. et Phys., (3), *62*, p. 90; 1861 and C. R. *104*, pp. 334-335; 1887.

that the effect of the chromium salt was due to its increasing the absorbing power of the exciting light. Crookes[17] agreed with Becquerel on the whole, and showed that alumina fractionated from chromium with extreme care was luminescent. He carefully determined the lines of the "alumina spectrum" but, later, finding that some crimson lines of his "alumina spectrum" faded when he used a new method of fractionation[18] he recognized that some of the lines, particularly in the deep red, might be due to chromium. After that, Schmidt[19] reached the following conclusions: (1) Carefully purified alumina is non-luminescent. (2) The addition of a small quantity of chromium salt to pure alumina causes the appearance of a red luminescence. Hence that luminescence must be due to chromium. (3) The addition of a small quantity of copper salt to pure alumina causes the appearance of a green luminescence. Hence the green luminescence of alumina obtained by igniting metallic aluminium (which usually contains a small quantity of copper) must be due to that metal. But these researches were qualitative.

The extensive researches of Wiedemann and Schmidt[20] had established the fact that the luminescent color of alumina mixed with $Fe_2O_3$, CuO, or $Mn_2O_2$ undergoes essential variation when changes are introduced in the calcination temperature and in the concentration of the active metal. Therefore, it does not seem safe in this case to consider the luminescent color as an unique criterion by which to identify the chief active agent.

From the foregoing the following facts may be gathered:

(1) Pure alumina is non-luminescent.

(2) The purification of alumina for this purpose is very difficult. So small a quantity of some impurity, that careful chemical analysis can scarcely detect it, may produce a bright luminescence.

(3) There are several adequate methods of purification. Lecoq and Schmidt succeeded in obtaining pure alumina, but Crookes and Becquerel did not.

(4) Some, at least, of the red lines observed by Crookes and Lecoq must be actually due to chromium. Among them,

(i) The doublet at 6942. and 6937. A.U.[21] (Its origin seems to have been the chief subject of the long discussion.)

[17] Crookes, W.; Chem. News, *55*, pp. 25-27, 56-62 and *56*, pp. 59-62; 1887.
[18] Crookes, W.; Chem. News, *56*, pp. 72-74; 1887.
[19] Schmidt, G. C.; Ann. d. Phys. u. Chem., *15*, pp. 622-633; 1904.
[20] Wiedemann, E. und G. C. Schmidt; Ann. d. Phys. u. Chem., *56*, pp. 201-254; 1895.
[21] Crookes, W.; Chem. News, *55*, pp. 56-62; 1887.

(ii) Line 6897., found by Lecoq[22] in the spectrum of gallium oxides mixed with chromium. It may be identical with the line 6895., found earlier by Crookes.[23]

(iii) Lines 6707 and 6598 which disappeared from Crookes' spectrum upon more careful fractionation.[24]

Comparing these lines, or to speak more exactly, centres of bands, with the crests of the bands characteristic of chromium as obtained by the present author, we find:—

| | $\lambda_1$ in A. U. | $\lambda_2$ in A. U. | $\lambda_2-\lambda_1$ in A. U. |
|---|---|---|---|
| | Crookes or Lecoq | Cr bands, Tanaka | |
| (i) | 6942 | 6944 | 2 |
| | 6937 | | – |
| (ii) | 6897 | 6897 | 0 |
| | 6707 | 6701 | -6 |
| (iii) | 6598 | 6605 | 7 |

Except for the value 6937, there is a correspondent for each one. The differences $\lambda_2-\lambda_1$ are not unreasonably large, if we consider that the wavelengths for (iii) represent the centres of diffused bands. As to 6937, it may be pointed out that there are series consisting of doublets, occurring in zinc sulphate mixed with manganese of which this may be a member.[25]

Besides these, the following centres of bands in the fractionated alumina spectrum and alumina-samaria spectrum as observed by Crookes[26] correspond closely to certain bands assigned by the present author to chromium:

| Crookes $\lambda_1$ | Tanaka $\lambda_2$ | $\lambda_1-\lambda_2$ in A. U. |
|---|---|---|
| 6795 | 6795 | 0. |
| 6773 | 6775 | 0. |
| 6514 | 6517 | 3. |

Many other lines found in Crookes' alumina spectrum must have been due to other sources not eliminated by the fractionation.

[22] Lecoq de Boisbaudran, C. R. *104*, pp. 1584-1585; 1887.
[23] Crookes, W.; Chem. News, *43*, pp. 237-239.
[24] Crookes, W.; Chem. News, *56*, pp. 72-74.
[25] Tanaka, *loc. cit.*
[26] Crookes, W.; Chem. News, *56*, pp. 59-62; 1887.

TABLE 2. *Corundum, Ruby and Spinel*

| Substance | Active Agents | Bands identified |
|---|---|---|
| Corundum I | Cr(14) | 6306, 6233(5), 6174(6), 6095, 6019, 5942(1), 5900, 5869(0), 5795(6), 5777(6), 5593(2), 5541(3), 5527(5), 5463. |
| | Sa(12) | 6405(3), 6333(6), 6280(8), 6204, 6117(8), 6039(1), 5820(2), 5753(2), 5686(4), 5675, 5622, 5417(8). |
| | Cu(3) | 6374(6), 5987(8), 5925(8). |
| | Fe(2) | 6067(0), 6000(2). |
| Corundum II | Cr(9) | 5966(4), 5867(0), 5836(7), 5775(6), 5715(6), 5593(2), 5544(3), 5460(3), 5340(9). |
| | Sa(5) | 6041, 5730(9), 5674(5), 5490(9), 5308. |
| | Fe(2) | 5624(3), 5504(7). |
| Artificial Ruby | Mn(12) | 5490(8), 5310(1), 5275(4), 5248(7), 5182(1), 5139, 5085(4), 5052(1), 5025, 5004(5), 4979(8), 4883. |
| | Cr(4) | 5382(0), 5340(9), 5218(1), 4945(7). |
| Spinel | Mn(13) | 5488, 5469(0), 5430(2), 5420(3), 5371, 5309(1), 5274, 5247, 5220, 5183(1), 5142(9), 5084, 5005. |
| | Fe(1) | 5343(2). |

## NOTES ON TABLE II.

CORUNDUM I. (from Craigmont, Renfrew county, Ontario.) It showed a faint greenish luminescence, not sufficiently bright for measurements, so it was ground into a fine powder and heated to red heat for about half an hour. The luminescence then obtained was red. Fourteen chromium, twelve samarium, three copper, and two iron bands were identified. The existence of the band 5925. is definite evidence for the presence of copper, since this band is not near any band of any other metal which can be expected to occur in corundum.

CORUNDUM II. (from Franklin, Macon county, North Carolina). It, like the preceding, had to be ground into fine powder and heated to a red glow in order to obtain a luminescence of sufficient intensity for measurements. Nine chromium, five samarium, and two iron bands were identified.

According to the results obtained for these two samples the chief active agents of the luminescence of corundum are chromium and samarium, while iron and sometimes copper plays a small part.

The occurrence of chromium and samarium as impurities in alumina has been recognized by many physicists and chemists, to say nothing of iron, which, of all metals, has the widest distribution. The occurrence of copper in aluminium ores is quite probable also; the metallic aluminium manufactured from such ores (for example that obtained by the electrolysis of the solutions of alumina infused cryclite, $Na_3AlF_6$) is known to include, usually, a small quantity of copper.

It is known[27] that alumina mixed with a small quantity of chromium, samarium, iron, or copper, without being calcined, shows a hardly observable or faint greenish luminescence, and that after heating to a red glow it begins to emit a red luminescence. This change is accentuated if the concentration of the active metal is small. Similar variation in luminescence color, upon the process of calcination, is observable in most samples of alumina, corundum, and ruby.[28] It was also true of the two samples of corundum just described.

[27] Wiedemann, E. und G C. Schmidt; Ann. d. Phys. u. Chem., *56*, pp. 201-254; 1895.
[28] Crookes, W.; Chem. News, *55*, pp. 25-27; 1886 and E. Becquerel, C. R., *104*, p. 554; 1887.

"ARTIFICIAL RUBY." This sample (from Eimer and Amend) was a dark brown substance with a red tint. It showed a beautiful green luminescence. Twelve manganese and four chromium bands were identified. Manganese must be the chief active agent in this case.

SPINEL. ($MgO.Al_2O_3$) is a natural magnesium aluminate. It is known that a small part of the MgO is often replaced by MnO or FeO, and a small part of the $Al_2O_3$ by $Cr_2O_3$ or $Fe_2O_3$. Two samples of spinel were at the author's disposal. One of them was a ruby spinel from Ceylon, and was almost non-luminescent in its original state. Since it was a registered article belonging to the department of mineralogy of Cornell University, it could not be calcined, and the present observations are confined to the other sample.

This sample came from Antwerp, New York. It had a white natural color, with a violet tint. Not being sufficiently luminescent, it was ground into fine powder and heated to red heat for about half an hour, when it showed a quite beautiful, yellowish green luminescence. Thirteen manganese bands were identified, and one iron band. The iron band might be attributed to chromium, which has a band at 5559., making $\lambda_3 - \lambda_1 = -4$. Of course it is difficult to determine the origin of one band alone. But at one time in the experiments with this sample, a crest was found at 5454., which is reasonably near to an iron crest at 5451., but not to any crest of manganese or of chromium. Since this band did not occur frequently enough, it was not included in the table, but its appearance is one ground for attributing 5545. to iron instead of to chromium.

According to Lecoq,[19] most spinels show red luminescence, but some, green; if we make artifical spinels mixed with traces of either manganese and chromium, we get green and red luminescence respectively. Hence he attributed the luminescence of spinels to those two metals, according to its color. The present result confirms his conclusion regarding spinels showing green luminescence.

As regards the other type of spinel, Crookes[20] drew a map of the luminescence spectrum of a sample showing crimson luminescence. Most of the bands he drew were too broad to be identified by the present method, but he mentioned one sharp line with a wave-length of 6857. The extrapolation of one of the chromium series previously recorded by the present author,[21] shows that this is the exact location of one of its members. Thus it is probable that the active agent in spinels showing red luminescence is chromium. This also agrees with Lecoq's conclusion.

PHYSICAL LABORATORY OF
CORNELL UNIVERSITY.
JUNE, 1923.

[19] Lecoq de Boisbaudran, C. R., *105*, pp. 261-262; 1887.
[20] Crookes, W.; Chem. News, *55*, pp. 25-27; 1887.
[21] Tanaka, *loc. cit.*

# INSTRUMENT SECTION

## THE MEASUREMENT OF TRANSMISSION IN INSTRUMENTS

By G. W. Moffitt and Paul B. Taylor

In an optical instrument the ability to transmit a high percentage of the light emanating from objects within the field of view and incident on the objective is a most desirable characteristic. For this reason, apparatus capable of giving reliable values of percentage transmission fills an important place in the well equipped optical testing laboratory. To designers in particular it is of value in ascertaining the relative merits of competing types.

On examining the various papers of recent years dealing with the subject, one obtains the impression that the practice has become quite general of placing a diffusely radiating extended source close to the entrance pupil of the instrument and comparing the brightness of this source with that of its image at the exit pupil of the instrument in question, using any convenient photometric device. The ratio of these two brightnesses is assumed to be the transmission factor, the reasoning evidently being that since the exit pupil is an image of the entrance pupil the two would be of the same brightness if the transmission were perfect and that in any case the difference would represent the absorption—an assumption not necessarily justifiable for actual cases, as we shall see.

Wright[1] has treated the subject along these lines, applying the polarization photometer as the measuring instrument. In an account of the methods used for the testing of binocular instruments at the Bureau of Standards, Smith[2] described apparatus of a simple nature also using the polarization photometer. Guild,[3] appreciating the possible effects of polarization in the instrument under examination on the readings of a polarization photometer, has gone to considerable lengths of complication in order to annul these spurious effects.

Now, while the polarization photometer is neat, compact and very useful in many instances, it would seem that these additional complications of the optical system and the precautions to be observed in their

[1] Journal Opt. Soc. of America, *2-3*, p. 65; 1919.
[2] Journal Opt. Soc. of America, *2-3*, p. 76; 1919.
[3] Transactions Opt. Soc., *23*, p. 205; 1921-1922.

use make it a rather unsuitable instrument for measuring the transmission factor of optical instruments in general.

Moreover, if we consider the general problem of the photometry of optical instruments in the laboratory it becomes obvious that many instances will arise requiring the use of a comparison source. This procedure is, of course, rather objectionable for the reason that twice as many photometric matches are necessary for a determination. Moreover, the possibility of differential fluctuations of the two lamps must be guarded against. But if it must be used in a number of instances, and especially if it leads to a simplification of apparatus, it may be that an instrument employing it in all cases would be most generally useful. Keuffel[4] has constructed apparatus of this kind in which an illuminometer working on the inverse square principle, and a diffusely radiating comparison source are fed from the same circuit.

But we still have for consideration the question of the validity of any method in which the exit pupil brightness is compared with that of the entrance pupil when one or the other is illuminated by a diffusely radiating source placed close at hand. Whenever light from an object within the field of view of a telescope enters the instrument a part of it is absorbed, a part thrown back into the object space, part is scattered to the side walls again to be scattered (some of it ultimately reaching the exit pupil), part is inter-reflected and makes itself evident as flare and ghosts (some of which also gets through the exit pupil), and the remaining part, passing out through the instrument in the way intended, goes to form the image of the object. Now, if the whole field of view be composed of luminous areas it is obvious that the amount of scattered light and flare ultimately passing through the exit pupil will be greatly increased. It will be still further increased if the radiating source shines into the entrance pupil from all angles within a hemisphere—as is apt to be approximately the case when the diffusely radiating illuminator is placed close to the entrance pupil. All this scattered light, which really adds nothing to the effective brightness of the image of objects observed through the telescope but which, in fact, serves to detract from the view by lowering the contrasts, increases the brightness of the exit pupil and therefore leads to a value for the transmission factor that is too high. Thus the possibility exists that an instrument with low transmission of image forming light but with a large amount of flare or scatter might be assigned a higher transmission factor than a superior instrument possessing these defects in lesser measure.

[4] Keuffel & Esser, Hoboken, N. J.

This objection to the entrance and exit pupil brightness method may be brought out emphatically by carrying the conditions to an absurd degree. Suppose the objective of the instrument to be left with a fine-ground surface. This would probably have only a small effect on the total transmission but would practically destroy its image forming properties. It is obvious that the transmission factor of such an instrument, as determined by the entrance and exit pupil brightness method, would be practically the same as for the instrument with a normal objective if the radiating source were close to the objective, and that generally it would be affected by the magnitude of the solid angle subtended by the source at the objective. It is also equally obvious that the image forming transmission of such an instrument would be vanishingly small. Since all optical surfaces scatter some of the light it follows that this phenomenon always exists to a greater or lesser degree.

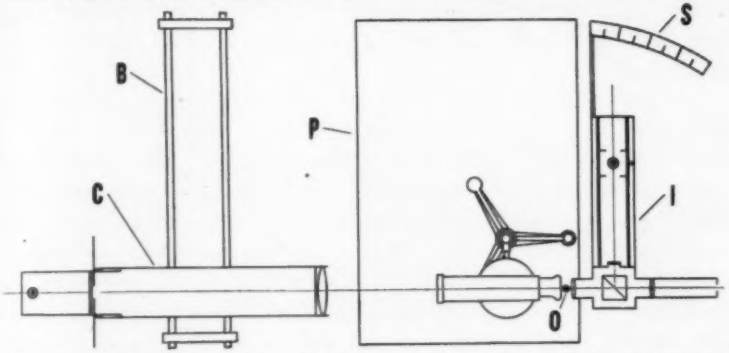


FIG. 1. *Diagram of transmission photometer. C, collimator. B, bench. P, instrument platform. I, illuminometer. S, scale. O, axis of rotation of platform and illuminometer.*

Considerations of this kind lead to the conclusion that the proper way to measure the transmission factor of an instrument is to compare the actual brightness of a distant object with the brightness of its image as seen through the instrument in question. Moreover, the object should be as small in angular extent as is convenient in the photometric process, and the objective of the instrument should receive no other light; that is, the field of the instrument should be dark. In order to make a comparative study of the two methods the devices to be described below were designed and constructed.

## APPARATUS

A transmission photometer arranged to meet the conditions outlined above is shown diagrammatically in Fig. 1. It consists essentially of a

collimator, $C$, which furnishes an effective distant source, a platform, $P$, on which to mount the instrument whose transmission is to be measured, and an illuminometer, $I$, modified by the addition of a short-focus objective and a ground glass exit pupil screen.

The collimator carries a 7.5 cm achromatic objective of about 45 cm focal length. The radiating disk of opal glass located at the principal focus of this lens is provided with a sliding diaphragm having holes of suitable diameters. These holes are so graduated as to enable one to compensate for the magnification of the instrument under test and thus maintain a desirable diameter of image in the field of view of the illuminometer.

Through the use of the collimator the large diffusely radiating source required for the entrance and exit pupil brightness method is done away with, and with it the difficulties of securing uniform illumination over a large area. Moreover, the complications introduced by inter-reflection between the source and the objective of the instrument are eliminated.

The collimator is mounted on a bench, $B$, along which it can be moved for the purpose of alignment with offset instruments.

In order to obviate the difficulty which might sometimes be experienced in finding the image and securing alignment quickly when handling high power instruments the following adjustments have been provided. The platform, $P$, which carries the instrument support, may rotate about a vertical axis through $O$ in Fig. 1. The instrument under test is to be so placed on its support that its exit pupil lies on this vertical axis, and also on the axis of the illuminometer. The support itself is provided with coarse and fine vertical motions, and it may be easily moved bodily on the platform for lateral adjustment. When these adjustments have been made the rotation of the platform about the axis $O$ produces a rotation of the instrument about its exit pupil. Means are provided for holding the various instruments: for the smaller ones V-blocks suffice, while for some of the larger ones, such as the battery commander's telescope, special supports have been provided (Fig. 2).

The illuminometer, $I$, modified by the addition of certain conveniences, contains the usual Lummer-Brodhun cube, comparison lamp, and scale. A simple shutter designed to cut off the light from the illuminometer lamp without disturbing any of the electrical contacts has been found to be very convenient for aligning an instrument for test. The principal modification of the illuminometer, however, consists

of an objective of about 7 cm focal length so arranged as to focus an image of the distant source in the field of view. Since the focal lengths of the objective and of the eyepiece are about the same, the magnification by the illuminometer is approximately unity, and its entrance and exit pupils of about the same diameter. (It will be noted that the entrance pupil of the illuminometer must be kept smaller than the exit pupil of any instrument to be tested.) The limiting stop of the whole optical system is a disk with a peep hole 2 mm in diameter and placed at the exit pupil of the illuminometer. This small diameter insures the same size of entrance pupil for the observer's eye both

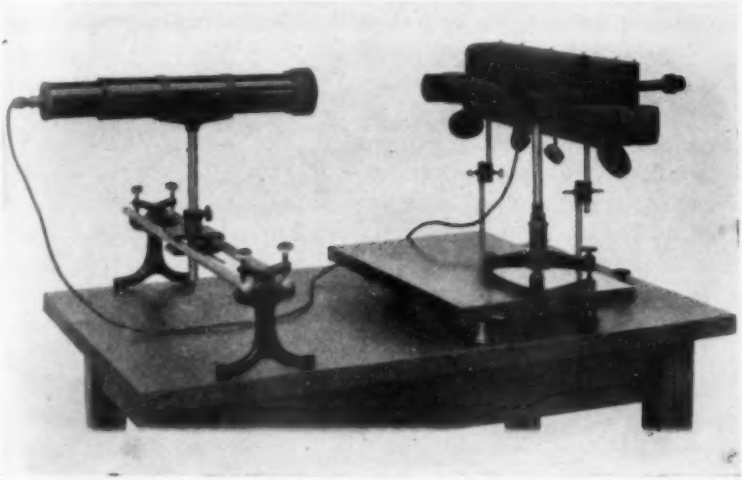

FIG. 2. *Transmission photometer showing collimator offset for measuring the transmission of a battery commander's telescope.*

with and without the instrument in the optical path. The disk forming the stop may be swung aside revealing a ground glass focusing screen (Fig. 3). In this screen is a hole slightly larger than the peep hole and concentric with its normal position. In case one should happen to get an instrument having an exit pupil so small that it would not fill the exit pupil of the illuminometer, the fact would be at once indicated by the failure of the disc of light to fill the hole through the ground glass.

The illuminometer is mounted so that it may be rotated about the axis, *O*, of the instrument platform, that is, about its own entrance pupil. It may also be moved a considerable distance laterally so that one may

look directly through the instrument under test for purposes of alignment. Since the exit pupil of the instrument and the entrance pupil of the illuminometer are coincident and lie on the vertical axis through the point $O$, either instrument platform or illuminometer may be rotated without disturbing the coincidence of these two pupils. A levelling screw in the base of the illuminometer enables one to make small changes in the angle of elevation of the illuminometer axis.

## PROCEDURE

In operation the collimator and illuminometer are first centered and aligned, a photometric match made, and the reading recorded, no instrument being in the optical path. The instrument whose trans-

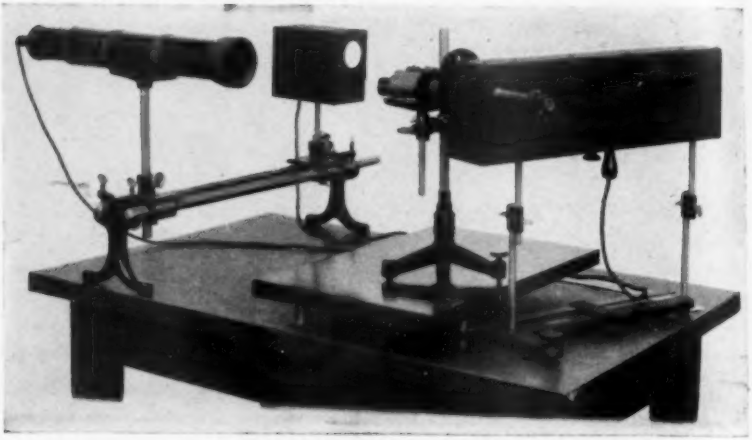

FIG. 3. *Transmission photometer showing the removable peephole disk and the exit pupil focusing screen.*

mission is to be measured is then introduced. If its entrance and exit axes are one straight line no further adjustment of collimator or illuminometer is necessary, and all centering may be done with the instrument stand. If difficulty is experienced in so aligning the instrument that the image is seen in the field of view of the illuminometer, the illuminometer may be moved aside laterally. Alignment for altitude can then be made by sighting directly on the collimator with one eye while sighting through the instrument with the other. The illuminometer is then returned to working position and if the image is not seen it may be brought into the field by simply rotating the

platform about the point *O*. Centering of exit pupil is then checked and corrected by means of the ground glass disk. When the image has been centered and a suitable stop placed in the collimator to give the desired size of image, a second photometric match is made. The square of the ratio of the two lamp distances is the transmission factor of the instrument.

If the instrument is direct vision but with an offset, it is necessary to move the collimator sidewise on the bench (but maintaining it parallel to its first position) until instrument and collimator objectives are centered (Fig. 2). This centering may be achieved sufficiently well by noting when the objective of the instrument is in the center of the spot of light which may be seen on a white card held in that locality.

For instruments of other forms the collimator and its bench may be moved with respect to the rest of the apparatus as the case may require.

Transmission factors for different parts of the field of view of an instrument may be measured by rotating the instrument platform and the illuminometer until the image occupies any position in the field of view of the instrument that may be desired. A scale is provided with which to read the illuminometer rotation, and from this the field angle for any setting may be determined provided the magnification of the instrument is known—as it usually is with sufficient precision for the purpose.

Transmission through different zones of an instrument may be measured by traversing so that different portions of the exit pupil are registered on the central hole of the ground glass exit screen.

In making the modifications in the illuminometer that have been described provision was made for quickly changing the apparatus to measure transmission factors by the entrance and exit pupil brightness method. For this purpose the original diffusely radiating illuminator was kept intact and the illuminometer was provided with a turret device for quickly changing from the objective to the clear glass entrance window. Thus an instrument might be measured by both methods in a comparatively short time.

## RESULTS AND CONCLUSIONS

One of the peculiarities of the entrance and exit pupil brightness method that impresses itself upon anyone attempting to use it for the first time is the variation in results obtained with a variation in the distance from the diffusely radiating source to the instrument. And

since there is no way of determining which distance gives the correct results there will remain considerable uncertainty about the values obtained. But with the focused image method distance of the collimator seems to play a negligible part within that considerable range of distances for which the system is properly filled. For a variation of this distance from .25 to 60 inches the results varied by only a fraction of one per cent.

In order to compare the results obtained with the two methods instruments of a variety of grades and types were examined. A well designed prism binocular in good condition gave values by the two methods agreeing within the uncertainties of the measurements. But if the distance of the source had been different in the diffusely radiating method the results would not have shown the agreement they did. A gun sight of good design gave a value 1.5% lower by the focused method than by the other, while another sight of inferior design and workmanship gave 51% by the focused method and 60.5% by the other. Thus it is seen that considerable differences may occur in the results by the two methods although for instruments of good grade the two methods agree fairly well.

Moreover, the straightforward step-by-step adjustment of the apparatus preparatory to taking a reading, and the ease with which one may satisfy himself that proper alignment prevails tend to make the focused image method the choice of systematic experimentors.

From the figures just given it is seen that the focused image method measures more nearly correctly the real image forming transmission and therefore gives what is wanted. With it a large amount of flare and scatter will not be mistaken for actual transmission of image forming light.

FRANKFORD ARSENAL,
PHILADELPHIA, PA.,
NOVEMBER, 1923.

# CALORIMETRY OF SATURATED FLUIDS*

By Nathan S. Osborne

Perhaps no single class of physical data finds more useful employment than the thermodynamic properties of fluids used in heat engines. In consequence, such data, in the working range of engineering practice, are highly valued, and the output of investigators has failed to keep pace with the needs which have arisen because of extension either of the variety of fluids so employed, or the working range of temperatures and pressures. It may be observed that as a source of precise knowledge of the thermal behavior of fluids there has been a tendency to favor measurements of the inter-relations of pressure, volume and temperature in preference to direct measurements of the capacity to absorb heat. It is possible that a well founded awe of direct calorimetric methods and the neglect of their study has hindered a due appreciation of the extent to which modern refinements in laboratory appliances and methods render calorimetry advantageous as a method of making a precise survey of the thermal behavior of a fluid.

The analysis of the calorimetric processes which have been employed in the experimental determination of the thermodynamic properties of saturated fluids is a special phase of the subject which has often been treated in a casual manner. The processes themselves are apt to be complicated owing to physical limitations in experimentation, affording temptation to make arbitrarily approximations and assumptions tending to simplify the theory. Furthermore the fact that work relative to the theoretical aspect of the subject has usually been published incidentally tends to keep it in obscurity.

The foregoing remarks are illustrated in the analytical portion of a series of papers,[1] of which the present writer was joint author, presenting measurements of specific heat and latent heat of ammonia.

In those investigations the analysis of the method of reduction of observations, though sufficiently rigorous for the precision of the experimental work, was not developed primarily as a guide in the experimentation. Later as a preliminary step in dealing with an analogous experimental problem, the improvement of the method of

* Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.

[1] Bulletin Bureau of Standards, *14*, pp. 133, 397, 433, 439; 1917. Scientific Papers Nos. 301, 313, 314, 315. Jour. Am. Chem. Soc. *40*, No. 1, pp. 1, 14; 1918.

analysis was undertaken, and the results of this revision form the nucleus of the present paper. The previous experimental work has, of course, furnished perspective for the subject of this paper.

It is a pleasure to acknowledge an obligation to Dr. Edgar Buckingham for suggestions found helpful in development of the analysis.

This paper deals with the theory of certain calorimetric processes for the determination of some of the important thermal properties of saturated fluids; and with the interpretation of the theory as bearing upon its experimental application.

Calorimetry of a fluid is the operation of measuring the heat exchanged between a quantity of fluid and other bodies when the fluid undergoes a definite change of state. Calorimetry of a *saturated fluid* is restricted to the processes in which both liquid and vapor are always present. Appropriate heat measurements, together with observations of temperature and pressure, are sufficient to evaluate a group of thermal properties of a saturated fluid over a wide range of conditions.

The analysis reveals that three particular types of calorimetric process, which may be performed separately in the same apparatus, make up a self sufficient experimental series. Three quantities, each characteristic of one of the processes, are determined by the measurements as functions of temperature or pressure. From these three characteristic functions alone most of the important properties of a saturated fluid are obtained directly, including the heat contents, entropies, specific heats, and specific volumes.

As a corollary of the analysis, and of previous experience, a few remarks are made upon refinements of experimental methods and equipment appropriate to this special branch of calorimetry.

## PHYSICAL BASIS OF THEORY

A brief outline description of experimental equipment and procedure may be given as a ground work for the analysis.

The fluid is to be enclosed in a container or shell made of a suitable, thermally conducting, elastic solid. The interior space is provided with a controllable means for introducing measured amounts of heat, such as an electric heater, and also with a stirrer or some other means for quickly distributing the heat added through the fluid in the enclosed space and to the solid parts. Outlets are provided for adding or withdrawing fluid. These outlets are provided with valves so that when desired the amount of fluid contents may be kept fixed.

For the purpose of avoiding unmeasured heat leakage the container is supported within an envelope. The thermal connection between the two is kept down by employing such refinements as vacuum insulation. The envelope is provided with temperature control so that the temperature difference between it and the container may be observed and kept small. In a complete experiment the slight outstanding thermal leakage may thus be evaluated. A thermometer is provided for indicating the temperature of the calorimeter system, consisting of the container and fluid contents, when it is in equilibrium. Detachable receivers connected to the outlets are located in an outer environment to hold the part of the fluid transferred to or from the calorimeter and to enable its mass to be determined by weighing.

If the necessary auxiliary devices are provided, the following quantities may be observed:

(1) Temperature of the container and fluid contents when in thermal equilibrium;

(2) Pressure of the vapor in the calorimeter at any instant;

(3) Initial and final mass of fluid in the calorimeter;

(4) Entire amount of heat added during any period of time, including that due to thermal leakage and energy dissipated in stirring. This will all be included in the term "heat added."

The system just described may be subjected to the following processes, each starting and ending with a condition of thermal equilibrium of the calorimeter and contents.

(1) By adding heat, without changing the amount of contents, the temperature may be raised from the initial to the final equilibrium value. This process is accompanied by changes in pressure, specific volumes, and relative proportions of vapor and liquid present; and also by changes in dimensions of the container due to change in temperature and corresponding pressure.

(2) The amount of the fluid contents may be either increased or decreased. This change may be accomplished by introducing or withdrawing either liquid or vapor. A final change in equilibrium temperature may or may not result depending on whether or not the heat of transformation is compensated by the addition of heat from without the system.

We shall first treat the second or general case in which both the mass of contents and the resultant temperature change. The general equation thus obtained will then, by proper specializations, be made applicable to the particular experimental processes which are finally

found to be useful. It is assumed that both liquid and vapor phases are present in the calorimeter throughout the entire process, and also that the temperature and pressure of the fluid transferred are identical with those at the free surface in the calorimeter. Departure from this latter condition will next be considered in more detail.

### REMARK ON STATE OF FLUID TRANSFERRED

In stating the experimental conditions for which the analysis was to be developed the temperature and pressure of fluid transferred were considered to be identical with those at the free surface. This simplifies the analysis but evidently the assumption only avoids immediate consideration of variations. This is an example of a vital though somewhat obscure element in the accuracy of an experimental determination, which may be dealt with in several contrasting ways. In lieu of testing the effect of the state of the fluid we might accept the results on faith, trusting that the discrepancies would be made negligible by judicious refinements in apparatus and manipulation, but in that event "reproducibility of results" should not necessarily be translated "reliability." In the present case two courses are open for making such a test.

In the first place we might undertake to determine the departures of the state of the transferred fluid from the assumed state of saturation by making instrumental provision for observing the temperature and pressure of the fluid in transit at the calorimeter boundary at any instant. Then the heat exchanged because of these departures could be expressed in terms of periodically observed values of the temperature and pressure, the rate of flow and the thermal properties of the fluid. If these quantities were sufficiently well known a correction term could be included in the calculation of results. Objections to this method are (a) limitations on the ability to observe the temperature and pressure of the fluid in transit, (b) necessity for supplementary knowledge of thermal properties of the fluid, (c) in the case of vapor, uncertainty of the quality even when pressure and temperature correspond to saturation. It is likely that in the usual course of the preparation of the apparatus, provision would be made for observing the temperature of the exit tubes and that the size of these would be so chosen that for the proposed rates of flow only a slight pressure drop would occur in the tubes within the limits of the calorimeter system. Such provision would be useful not only as a check on the state of the transferred fluid, but in other ways.

The second method, which seems to be preferable, is based on the principle that whether due to defects in *pressure*, *temperature*, or *vapor quality*, the resultant defect in heat from that called for by the equation will approach zero as the rate of transfer is diminished. To establish this principle one first notes that saturated vapor means vapor in equilibrium with the liquid phase. Furthermore, a calorimeter provided with adequate heat distributing means and an adiathermically operated envelope tends, with its contents, to approach equilibrium of temperature and pressure when left to itself. Consequently, departures of *temperature* and *pressure* from equilibrium values will diminish as the process to which temperature and pressure changes are due is retarded, that is as the withdrawal of fluid and compensation of the heat of vaporization by added heat are made slower. Considering a departure in *quality* from *dry saturated vapor*, whether it is due to mechanically entrained drops initiated by active boiling of the fluid, or in case of quiet evaporation, to a transition from the liquid to the vapor phase so gradual that it is still incomplete when the vapor is withdrawn,—in either case the magnitude of the defect in quality will be less the slower the process. Hence in carrying out experiments involving fluid transfer in apparatus and by manipulation already refined to approximate as closely as possible to the ideal conditions of equilibrium, if the rate of transfer be varied within reasonable limits, we have in the comparison of the results a means of test of the actual influence of the departures from the ideal, and by choice of a suitable rate a means of control of the effect to limits within tolerance.

### REMARK ON OBSERVATION OF PRESSURE

It should be noted here that although the vapor pressure has been specified for observation, it does not follow that for the sole purpose of reducing the calorimetric data the absolute pressure must be determined to the highest possible accuracy. Indeed for the conditions most likely to be experienced, moderate absolute accuracy would suffice. But it may be remarked that the means for control of the fluid which have been specified primarily for the calorimetric measurements make it possible to observe the vapor pressure under conditions very favorable for high accuracy. This is especially true if adequate mechanical stirring is provided, since that operation tends to keep the surface fresh and thereby lessens the influence of slight impurities on the pressure. Furthermore when dealing with saturation conditions, convenience alone determines whether temperature or pressure shall

be used as an independent variable in expressing the measured heat quantities and their derivatives. The question of relative convenience or accuracy of these two observations is purely one of technique, to be considered in connection with a particular experimental project; but in any event the expediency of observing *both temperature* and *pressure* with an accuracy appropriate to their use as primary variables should evidently receive careful consideration.

It will be shown later that if *both* temperature and pressure are observed, then these data together with the quantities of heat which it is proposed to observe permit us to evaluate the *specific volumes* of the *saturated fluid* in addition to those properties which may otherwise be derived.

## THEORY

### Notation

$M$ = Mass of fluid contents of calorimeter. A particular time or state is denoted by subscripts.

$\theta$ = Temperature on the thermodynamic scale. Subscripts 1 and 2 denote initial and final equilibrium temperatures of calorimeter and contents. Unless otherwise specified, $\theta$ denotes instantaneous temperature of free surface of fluid in calorimeter.

$\pi$ = Pressure of vapor in equilibrium with liquid at temperature $\theta$.

$P$ = External pressure on calorimeter.

$V$ = Internal volume or capacity of calorimeter.

$V_A$ = External volume of calorimeter.

$u$ = Specific volume of saturated liquid.

$u'$ = Specific volume of saturated vapor.

$x$ = Fraction of fluid contents of calorimeter which is vapor. Quality factor.

$Q$ = Net heat added to calorimeter and contents, including electric power input, thermal leakage, and heat dissipated in work of circulating fluid.

$W$ = Work done by external forces on calorimeter and contents.

$\delta M$ = Any infinitesimal element of mass of fluid transferred to calorimeter.

$\delta W$ = Work done upon the fluid in the calorimeter by external forces by transfer of element $\delta M$.

$y$ = Fraction of an element $\delta M$ which is vapor. In the present discussion, $y$ is presumed to be either 1 or 0.

$L$ = Heat of vaporization of unit mass of fluid.

$E$ = Internal energy of calorimeter and contents.

$E_A$ = Internal energy of calorimeter.

$E_x$ = Internal energy of contents.

$\delta E_y$ = Internal energy of an element $\delta M$ of fluid transferred to calorimeter.

$\epsilon$ = Internal energy of unit mass of saturated liquid.

$\epsilon'$ = Internal energy of unit mass of saturated vapor.

$H$ = Heat content of saturated liquid per unit mass referred to the value at some arbitrary temperature $\theta_0$ as zero. $H$ is defined by the relation $dH = d\epsilon + d(\pi u)$.

$H'$ = Heat content of saturated vapor referred to same zero point as $H$. $H' = H + L$.

$q$ = Heat added to unit mass of saturated liquid in a reversible process.

$q'$ = Heat added to unit mass of saturated vapor in a reversible process.

$\phi$ = Entropy of saturated liquid.

$\phi'$ = Entropy of saturated vapor.

$\sigma$ = Specific heat of saturated liquid $\left(\frac{\delta q}{\delta \theta}\right)$

$\sigma'$ = Specific heat of saturated vapor $\left(\frac{\delta q'}{\delta \theta}\right)$

## DERIVATION OF GENERAL EQUATION

The purpose of the analysis which follows is to formulate the relations between the quantities observed in the experiment and the properties of the fluid which are to be determined. Of the things which happen in the experiment, those which most directly affect the analysis will be recalled in order better to fix them in mind. A measured quantity of heat is added and distributed to the calorimeter and its fluid contents, and at the same time fluid is gradually transferred. These two actions are under the control of the operator, and in principle each may be treated as though it could go on in either direction. As a result of these two operations a change occurs in the state of the calorimeter and the fluid within it. As an accompaniment to this change of state, work is done on or by the system against external forces. The change in state is determined by suitable observations and this together with the observed migration of the fluid gives a basis of accounting in terms of external work and internal energy for all the measured energy added in

the form of heat. This accounting utilizes the principle of conservation of energy and is the first step in the analysis.

As a matter of convenience we shall define the system to which the principle is to be applied as that space within which we may account by observation for heat added, amount and state of matter, and work done. It will be seen that this definition describes the calorimeter and its contents, a system which, it is true, changes in mass but for which the energy account may nevertheless be made up. In the present analysis we shall disregard all changes of energy within the system other than measured heat added, external work done or change of internal energy. Having thus defined the system, it follows from the principle of conservation that whatever energy is added to the system either as heat, work done or internal energy of fluid introduced, must appear as an increase of the internal energy of the system in its final state of equilibrium over that in its initial state. In terms of the symbols adopted this statement may be written in the form

$$[Q]_1^2+[W]_1^2+\int_1^2\delta E_y=[E_A]_1^2+[E_x]_1^2 \tag{1}$$

The internal energy $E_x$ of any mass $M$ of the fluid of quality $x$ may be expressed in terms of the internal energy per unit mass of the liquid and the vapor. The amount of liquid present is $M(1-x)$ and the internal energy of each unit of mass is $\epsilon$. The amount of vapor is $Mx$ and its internal energy per unit mass is $\epsilon'$. Hence the internal energy of the whole mass $M$ may be written

$$E_x=M(1-x)\epsilon+Mx\epsilon' \tag{2}$$

or by rearrangement

$$E_x=M\{\epsilon+x(\epsilon'-\epsilon)\} \tag{3}$$

Similarly the internal energy of an element $\delta M$, of quality $y$, may be written

$$\delta E_y=\{\epsilon+y(\epsilon'-\epsilon)\}\delta M \tag{4}$$

Since the various internal energy elements appear in the present analysis only in intermediate steps where numerical evaluation is not required, it is not necessary to introduce an arbitrary constant as a reference value, but only to mention that all the elements of internal energy are referred to the same state as zero.

Turning to the work done on the system—that done against the constant and uniform external pressure $P$ by reason of the change in external volume of the container is equal to $-[PV_A]_1^2$. The only other external work during the experiment is that which accompanies the transfer of fluid. The work $\delta W$ done on the system when any element

$\delta M$ is transferred to it is equal to the product of the instantaneous pressure $\pi$ by the corresponding volume transferred. In terms of the specific volumes and the quality factor $y$, $\delta W$ may be written

$$\delta W = \pi[u(1-y)+u'y]\delta M \tag{5}$$

or by rearranging

$$\delta W = \pi[u+y(u'-u)]\delta M \tag{6}$$

The whole external work $[W]_1^2$ done on the system during an experiment is therefore

$$[W]_1^2 = -[PV_A]_1^2 + \int_1^2 \pi[u+y(u'-u)]\delta M \tag{7}$$

Substituting from (3) (4) and (7) into (1) and rearranging we now have

$$[Q]_1^2 = [E_A+PV_A]_1^2 + [M\epsilon+Mx(\epsilon'-\epsilon)]_1^2 - \int_1^2 \{\epsilon+\pi u+y[(\epsilon'-\epsilon) + \pi(u'-u)]\}\delta M \tag{8}$$

This equation may be simplified by use of the relations[2]

$$Mx = \frac{V-Mu}{u'-u} \tag{9}$$

$$\epsilon'-\epsilon = L-\pi(u'-u) \tag{10}$$

$$H = \epsilon+\pi u+K \tag{11}$$

Multiplying (9) by (10) gives us

$$Mx(\epsilon'-\epsilon) = \frac{V}{u'-u}L - V\pi - M\frac{u}{u'-u}L + Mu\pi \tag{12}$$

and upon substituting from (10), (11) and (12) into (8) and rearranging, we have finally

$$[Q]_1^2 = \left[E_A+PV_A-\pi V+\frac{V}{u'-u}L\right]_1^2 + \left[M\left(H-\frac{u}{u'-u}L\right)\right]_1^2 - \int_1^2 (H+yL)\delta M \tag{13}$$

## PRELIMINARY DISCUSSION OF GENERAL EQUATION

We now have in equation (13) an expression for the heat added in a complete experiment of the general type, and this general equation is in a convenient form for physical interpretation; for the second member shows how the added heat is distributed with reference to, (a) the quantity and state of the fluid during the experiment, (b) the properties of the fluid, and (c) the characteristics of the container.

The first term of the second member is independent of the amount of fluid contents, except that enough fluid must always be present to insure the saturation condition. For a particular instrument and a

[2] The $K$ in (11) is merely a constant of integration of the differential equation by which the heat-content $H$ is defined and its value does not interest us since it promptly cancels out.

particular fluid the value of the quantity, $E_A+PV_A-\pi V+\frac{V}{u'-u}L$, is completely determined by the temperature. Except for possible slight variations such as might be caused by change in external pressure $P$, by hysteresis effects on the volume $V$, or by the average internal pressure not being exactly equal to $\pi$, all exceptions of no practical consequence, this expression is a thermal characteristic of the calorimeter as actually used, and it is analogous to thermal capacity though not precisely equal to that property as ordinarily determined. In what follows this expression will be denoted by the symbol $Z$ and regarded as a function of temperature. As will be seen later it may be used in the reduction of experimental results without any more explicit interpretation.

The second trem is completely determined by the properties of the fluid, and the initial and final states of equilibrium. It is independent of the nature of the intermediate process and of the characteristics of the instrument. The value of the expression $H-\frac{u}{u'-u}L$ is a thermal characteristic of the fluid. Both this quantity and $Z$ will presently be expressed in terms of measured quantities of heat.

The third or last term alone deals with the heat concerned in the transfer of fluid during the experiment. Its value is evidently determined by the state of the free surface of the fluid, by the rate of transfer, and by the type of experiment denoted by the quality factor, $y$.

Without further discussion of this equation for the general type of experiment we shall now proceed to apply it to the several particular experimental processes which are to be examined.

## CONSTANT MASS EXPERIMENTS

Considering first the process in which the fluid contents remain unchanged in amount during an experiment, equation (13) reduces to the form

$$[Q]_1^2=[Z]_1^2+M\left[H-\frac{u}{u'-u}L\right]_1^2 \tag{14}$$

Now let $M_a$ and $M_b$ denote the masses of the contents in two separate experiments, in each of which the temperature of the calorimeter and contents is changed from $\theta_1$ to $\theta_2$. Let $[Q_a]_1^2$ and $[Q_b]_1^2$ denote the measured quantities of heat added in the separate experiments. Solving the two simultaneous equations which are thus obtained for $H-\frac{u}{u'-u}L$ results in the following equation

$$\left[H-\frac{u}{u'-u}L\right]_1^2=\frac{[Q_b]_1^2-[Q_a]_1^2}{M_b-M_a} \tag{15}$$

This equation is adapted to the determination of the change in the quantity $H-\frac{u}{u'-u}L$ as a function of temperature, from two series of experiments. This quantity is thus seen to be a function the form of which is *characteristic of this particular type of experimental process*. For accuracy, $M_b-M_a$ should evidently not be too small.

If the quantity $\frac{u}{u'-u}L$ is also known as a function of temperature, the heat content, $H$, of the saturated liquid is at once obtained by addition, thus making it possible to determine $H$ by the type of calorimetric measurement discussed above. But $\frac{u}{u'-u}L$ may also be determined by a direct calorimetric measurement of another type to which the general equation (13) is applicable, and which will be discussed a little later. (As an alternative method, $\theta u\frac{d\pi}{d\theta}$, the thermodynamic equivalent of $\frac{u}{u'-u}L$, may be computed from already known data for $u$, $u'$, $\pi$ and $L$. The relative advantages of the two methods of determining the quantity $\frac{u}{u'-u}L$ will depend upon the range in which it is to be evaluated, availability of data, comparative precision, and convenience).

Before proceeding with the discussion of the two additional types of experiment to which equation (13) is to be applied, we may consider how $Z$ is determined. The value of this quantity is required in the reduction of the results of these other types of experiments on account of the practical difficulty of terminating an experiment at precisely the starting temperature, as would be necessary to make $[Z]_1^2$ vanish.

The quantity $Z$ may be obtained as a function of temperature from the two series of experiments each with constant $M$, already discussed, in the following manner. Returning to equation (14) first divide through by $M$, let $M$ take two different values as above, and then solve for $[Z]_1^2$, obtaining the equation

$$[Z]_1^2=\frac{[Q_b]_1^2M_a-[Q_a]_1^2M_b}{M_b-M_a} \tag{16}$$

which is adapted to the determination of $Z$ as a function of temperature from the series of experiments.

It is to be noted that in the determination of the two quantities $H-\frac{u}{u'-u}L$ and $Z$ from the two series of experiments it will ordinarily be necessary to interpolate from the actual value of the $Q_a$'s or $Q_b$'s as observed in order to express both for the same change in temperature $\theta_1$ to $\theta_2$. This is on account of the practical impossibility of exactly reproducing the same series of terminal temperatures $\theta_1$, $\theta_2$, $\theta_3$, etc. in two separate series of measurements.

## LIQUID WITHDRAWAL EXPERIMENTS

Returning to equation (13), let us consider its application to the calorimetric process leading to the determination of the quantity $\frac{u}{u'-u}L$. It will be found that this process is the one in which saturated liquid is transferred, and the condition which must be introduced into equation (13) is that $y=0$. Making this substitution and expanding, we have

$$[Q]_1^2=[Z]_1^2+M_2\left(H-\frac{u}{u'-u}L\right)_2-M_1\left(H-\frac{u}{u'-u}L\right)_1-\int_1^2 H\delta M \qquad (17)$$

Adding to (17) the identity

$$O=-M_2\left(H-\frac{u}{u'-u}L\right)_1-M_2\left(\frac{u}{u'-u}L\right)_1+M_1H_1+\int_1^2 H_1\delta M \qquad (18)$$

and cancelling, we have

$$[Q]_1^2=[Z]_1^2+M_2\left[H-\frac{u}{u'-u}L\right]_1^2-(M_2-M_1)\left(\frac{u}{u'-u}L\right)_1 -\int_1^2(H-H_1)\delta M \qquad (19)$$

and solving (19) for $\left(\frac{u}{u'-u}L\right)_1$

$$\left(\frac{u}{u'-u}L\right)_1=\frac{1}{M_2-M_1}\left\{-[Q]_1^2+[Z]_1^2+M_2\left[H-\frac{u}{u'-u}L\right]_1^2 -\int_1^2(H-H_1)\delta M\right\} \qquad (20)$$

## REMARK ON EVALUATION OF CORRECTION TERMS

Of the quantities in equation (20), $M_1$, $M_2$ and $[Q]_1^2$ are directly observed in the experiment, $[Z]_1^2$ and $\left[H-\frac{u}{u'-u}L\right]_1^2$, (the latter two usually small correction terms) are obtained from the results of experiments of the type previously treated, leaving the last term,

$\int_1^2 (H-H_1)\delta M$ still to be evaluated in order to complete the determination of $\frac{u}{u'-u}L$.

Consider now an ideal experiment in which the rate of transfer of liquid and the rate of adding heat are so perfectly correlated, and the distribution of heat throughout the entire system so nearly instantaneous that the temperature of the free surface never departs from the initial equilibrium temperature. In such an experiment $\theta$ is constant and equation (20) reduces to the form

$$\left(\frac{u}{u'-u}L\right)_\theta = -\frac{[Q]_1^2}{M_2-M_1} \tag{21}$$

It is obvious that the last three terms in equation (20) which are thus annulled must express the amount of heat added per unit of mass transferred by reason of the departure of the actual experiment from the ideal one. Since the quantities $[Z]_1^2$, $\left[H-\frac{u}{u'-u}L\right]_1^2$, $M_1$ and $M_2$, deal only with terminal conditions and involve only quantities observed either in this or in other coordinate experiments, their direct evaluation presents no difficulty. With the last term, $\int_1^2 (H-H_1)\delta M$, this is not true because its evaluation involves the instantaneous surface conditions, the instantaneous rate of transfer, and their relation to each other. Two methods are available for dealing with this quantity, but they will be merely outlined here because the final evaluation depends on experimental details.

One method is to evaluate the quantity in terms of periodically observed experimental conditions and their empirical relations, and to include it in the calculation.

The other is to reduce it to insignificance, by establishing limits on the variability of the instantaneous conditions of the experiment and then by suitable means, restricting the experiment within these limits.

Since there is no convenient way of observing the temperature of the free surface directly, the vapor pressure, $\pi$, which can be indicated instantaneously is the appropriate independent variable in terms of which either to evaluate or control the variation of the surface condition. The more perfect the control of the experiment the less $\pi$ will vary and the smaller $H-H_1$ will be. When small, $H-H_1$ can be expressed empirically in terms of $\pi-\pi_1$ with considerable accuracy even before the final value of the relation between $H$ and $\pi$ is established. By making proper instrumental provision for the purpose, the rate of transfer

of liquid can be made proportional to a pressure drop which can be observed or controlled. The entire term in question can be expressed in terms of pressure and time in such a way as to permit its evaluation by periodic pressure observations. It might be necessary to resort to successive approximations in special cases where the conditions of the experiment are unfavorable. A possible method of controlling the instantaneous pressure is suggested in a subsequent paragraph. At present there does not appear to be any insuperable difficulty in the practical disposition of this detail of the numerical reduction of results and we may return to the more general features of the analysis.

## VAPOR WITHDRAWAL EXPERIMENTS

For experiments in which fluid is transferred as vapor the method of reduction will be deduced by a process similar to that given for liquid transfer. The condition is that $y=1$. Making this substitution, noting that $H'=H+L$, and denoting heat added during vapor transfer by $Q'$, we find that equation (13) takes the form

$$[Q']_1^2=[Z]_1^2+(M_2-M_1)\left(H-\frac{u}{u'-u}L\right)_1+M_2\left[H-\frac{u}{u'-u}L\right]_1^2 -\int_1^2 H'\delta M \tag{22}$$

But since $(H+L)_1=H_1'$

$$\int_1^2 H'\delta M=(M_2-M_1)\,(H+L)_1+\int_1^2(H'-H_1')\delta M \tag{23}$$

By substitution from (23) into (22)

$$[Q']_1^2=[Z]_1^2+M_2\left[H-\frac{u}{u'-u}L\right]_1^2-(M_2-M_1)\left(\frac{u'}{u'-u}L\right)_1^2 -\int_1^2(H'-H_1')\delta M \tag{24}$$

whence by solving for $\left(\frac{u'}{u'-u}L\right)_1$

$$\left(\frac{u'}{u'-u}L\right)_1=\frac{1}{M_2-M_1}\left\{-[Q']_1^2+[Z]_1^2+M_2\left[H-\frac{u}{u'-u}L\right]_1^2 -\int^2(H'-H_1')\delta M\right\} \tag{25}$$

The previous discussion of the evaluation of the correction terms for experimental variability, in the reduction of equation (20) to obtain $\frac{u}{u'-u}L$ applies equally well to the determination of $\frac{u'}{u'-u}L$ from equation (25), since the equations are similar in form.

## RESUMÉ OF GENERAL THEORY

From the foregoing discussion of the general equation (13) it now appears that three quantities, all expressed in terms of specific thermal

properties of a particular fluid under saturation conditions, are completely determined as functions of temperature by the three calorimetric processes which have been discussed. Since each of these functions expresses the result of a particular type of calorimetric process, they may be regarded as fundamental calorimetric functions, and if we adopt the notation[3]

$$H-\frac{u}{u'-u}L=\alpha \tag{26}$$

$$\frac{u}{u'-u}L=\beta \tag{27}$$

$$\frac{u'}{u'-u}L=\gamma \tag{28}$$

we have

$$H=\alpha+\beta \tag{29}$$

$$L=\gamma-\beta \tag{30}$$

$$\frac{u'}{u}=\frac{\gamma}{\beta} \tag{31}$$

This completes the analysis in so far as it is concerned with the quantities of heat which are directly measured in the experiments and the thermal properties which are most directly derived from them by use only of the first law of thermodynamics. There are, however several other useful thermal properties which may be derived from the same group of heat measurements supplemented only by thermodynamic relations which involve the second law. The method of derivation of this coordinate group of thermal properties follows next.

## DERIVATION OF ENTROPIES AND SPECIFIC HEATS

Two relations involving the second law of thermodynamics are employed in expressing the entropies and specific heats of a saturated fluid in terms of the three characteristic calorimetric functions $\alpha$, $\beta$ and $\gamma$. The first of these relations when expressed in the notation for a

[3] It may be noted that since $\frac{u}{u'-u}$ and $\frac{u'}{u'-u}$ are pure ratios while $L$ is a physical quantity whose absolute magnitude may be determined by experiment, the quantities $\beta$ and $\gamma$ may be numerically evaluated without regard to any zero datum. The quantity $\alpha$, on the contrary contains the quantity $H$ involving the internal energy of unit mass of the fluid which we are able to evaluate only with respect to some arbitrarily chosen reference value. Consequently where the symbol $\alpha$ is used, an arbitrary constant is tacitly understood which is the same as that for $H$.

saturated fluid may be written as the following equation[4] for the liquid

$$\delta H = \theta\delta\phi + u\delta\pi \tag{32}$$

The other relation, known as Clapeyron's equation, may be written

$$\delta\pi = \frac{L}{\theta(u'-u)}\delta\theta \tag{33}$$

or in the notation of (27)

$$\delta\pi = \frac{\beta}{u\theta}\delta\theta \tag{34}$$

To express the entropy $\phi$ of the saturated liquid in terms of $\alpha$ and $\beta$ we have from (32)

$$\delta\phi = \frac{\delta H}{\theta} - \frac{u}{\theta}\delta\pi \tag{35}$$

and taking $H$ from (29) and $\delta\pi$ from (34) we have

$$\delta\phi = \frac{\delta(\alpha+\beta)}{\theta} - \frac{\beta}{\theta^2}\delta\theta = \frac{\delta\alpha}{\theta} + \delta\left(\frac{\beta}{\theta}\right) \tag{36}$$

whence for a finite change

$$[\phi]_1^2 = \int_1^2 \frac{\delta\alpha}{\theta} + \left[\frac{\beta}{\theta}\right]_1^2 \tag{37}$$

The entropy of vaporization, $\frac{L}{\theta}$ may be written, by (30)

$$\frac{L}{\theta} = \frac{\gamma-\beta}{\theta} \tag{38}$$

The entropy $\phi'$ of the saturated vapor is the sum of the entropy of the saturated liquid $\phi$, and the entropy of evaporation $\frac{L}{\theta}$; and taking

[4] That equation (32) is merely the combined statement of the first and second laws for a saturated fluid subjected to a reversible change of state may easily be verified as follows:

For a liquid subject to no outside force except its own vapor pressure $\pi$, the first law states that

$\delta\epsilon = \delta q - \pi\delta u$

where $q$ is heat added per unit mass, $u$ the specific volume and $\epsilon$ the internal energy per unit mass. For a reversible change or for any infinitesimal change from a state of equilibrium the second law states that

$\delta q = \theta\delta\phi$

where $\phi$ is entropy of the liquid per unit mass. Hence the equation

$\delta\epsilon = \theta\delta\phi - \pi\delta u$

is a combined statement of both laws for reversible changes in a saturated liquid.

And since by definition

$\delta H = \delta\epsilon + \delta(\pi u)$

by substitution equation (32) follows as above.

the values of these quantities from (37) and (38) we have

$$[\phi']_1^2 = \int_1^2 \frac{\delta a}{\theta} + \left[\frac{\gamma}{\theta}\right]_1^2 \tag{39}$$

Proceeding next to obtain expressions for the specific heats, since $\delta q = \theta \delta \phi$ in a reversible change, it follows that the specific heat of the saturated liquid, defined by the expression $\frac{\delta q}{\delta \theta}$, and denoted by the symbol $\sigma$, may be derived directly from equation (36), thus

$$\sigma = \frac{\delta a}{\delta \theta} + \theta \frac{\delta}{\delta \theta}\left(\frac{\beta}{\theta}\right) \tag{40}$$

and in a similar manner the specific heat of the saturated vapor $\frac{\delta q'}{\delta \theta}$, denoted by $\sigma'$ may be derived directly from the differential form of equation (39) thus

$$\sigma' = \frac{\delta a}{\delta \theta} + \theta \frac{\delta}{\delta \theta}\left(\frac{\gamma}{\theta}\right) \tag{41}$$

## DERIVATION OF SPECIFIC VOLUMES

It has been noted that if we observe the vapor pressure in addition to the other quantities, or if it happens to be known already as a function of temperature, we may then evaluate the specific volumes of the saturated fluid by using it in conjunction with the calorimetrically measured quantities $\beta$ and $\gamma$. Derivation of the expressions for this purpose makes use of Clapeyron's equation, (34) which has been used in the foregoing section. By solution of equation (34) for $u$ we have

$$u = \frac{\beta}{\theta \frac{\delta \pi}{\delta \theta}} \tag{42}$$

and by (31) we have

$$u' = \frac{\gamma}{\theta \frac{\delta \pi}{\delta \theta}} \tag{43}$$

The accuracy with which $u$ or $u'$ can be determined by this means is of course limited by the accuracy with which the several factors can be determined by the experiments, and it is evident that in the case of a liquid at moderate temperature and pressure such for instance as water between the ice and steam points, other more familar methods would be capable of far greater accuracy. But aside from that limitation the method has certain advantages which adapt it to the general survey of thermodynamic behavior of fluids for engineering purposes. The chief

advantage lies in the fact that the volumetric calibration of a container is obviated, an experimental operation attended with especial difficulty at extraordinary temperatures and pressures. In determining the *vapor volume* the proposed method has the advantage that the experiments may be carried out under *actual saturation conditions* whereas direct determinations of saturated vapor volumes are usually made by extrapolating to the saturation limit from observations made at a small degree of superheat. Furthermore the proposed method contemplates a thorough circulation and thus avoids much of the difficulty which attends direct observation of vapor pressure or specific volume because of the retardation of equilibrium by traces of impurity in the fluid when no means are provided for stirring.

It may be noted that when we determine specific volumes by use of Clapeyron's equation in the manner indicated we are merely reversing the procedure frequently used to evaluate the heat of vaporization of a fluid when the temperature, pressure and vapor volume have been observed. It may now be seen that observations made in a single instrumental set up suffice to complete the evaluation of the entire group of thermal properties of a saturated fluid, in a manner which not only is consistent thermodynamically, but in which an accuracy may be possible which is consistent with the use of the several properties in engineering calculations.

If it should be found expedient to determine the capacity of the calorimeter as a function of temperature and pressure, then it would be possible to use this capacity as a measure for determining the specific volume of the liquid and thus furnish a valuable check on the accuracy of the results.

## Remarks on Experimental Arrangements and Methods

One important use of such an analysis as the foregoing is to guide us in developing an experimental project for measuring a particular group of physical properties. The appropriate experimental conditions and the most advantageous experimental procedure may be predicted by using the analysis in conjunction with a knowledge of the practical possibilities and limitations of the experimental arts. The interpretation of the analysis may establish an ideal scheme as a goal toward which the development of ways and means may be directed, and it sometimes happens that setting up such an ideal results in the overcoming of difficulties which but for the ideal would have seemed too formidable for the experimenter to engage.

The following remarks have been prompted by the preliminary consideration of a particular experimental project, namely the determination of the properties of saturated water for the purpose of steam table revision; but most of them, like the foregoing analysis, are general and applicable to any saturated fluid. While the suggestions as to experimental refinements are intended to be practical, they should be accepted or rejected at their face value, that is as general principles until their practicability is demonstrated.

Were it not for the peculiarly special nature of the calorimetric processes discussed, that is, restriction of the fluid to the saturation condition, generally requiring restraint of the fluid within a closed system at extraordinary pressure, some of the remarks respecting instrumental refinements might appear obsolete, but as it is, some of the problems arising from the adaptation of familar calorimetric devices to this peculiarity still afford full scope for both ingenuity and inspiration.

## CONSTANT MASS EXPERIMENTS

The most obviously useful deduction from the analysis is the one concerning the heat capacity of the calorimeter itself.

Equations (15) and (16) tell in symbolic language exactly what calorimetric observations determine the quantities characteristic both of the saturated fluid and of the instrument during a change from one state of equilibrium to another.

In contrast with the usual method in which the thermal capacity of the empty calorimeter and of the calorimeter containing a known mass are determined separately and the thermal capacity of the fluid found by difference, these equations are applicable when thermal capacity determinations are made with the calorimeter containing two different known amounts of the saturated fluid, and they give by difference the thermal capacity of the amount of fluid by which the contents is altered. One advantage of this procedure is that in the reduction of the observations, neither the volume nor the thermal capacity of the calorimeter alone need be known, since the function $Z$ accounts for this characteristic of the instrument in the entire group of experiments. It is necessary however that with a given fluid the volume and thermal capacity be completely determined by the state of the fluid, and for this reason a *thermally conducting elastic* solid is specified for the material of the container. Any apparent novelty of the method consists in applying to a closed calorimeter system under considerable pressure the familiar principle of eliminating an unsought constant by taking

differences. The full advantage of the method is realized if adequate mechanical circulation is used to distribute heat added, because both determinations of thermal capacity are then made under equally favorable conditions as regards distribution of heat, which is not true for a determination when the calorimeter is entirely empty. The proposed method also has the advantages of simplicity in reducing observations, and greater consistency in the experimental precision.

## FLUID WITHDRAWAL EXPERIMENTS AND THE ADVANTAGE OF STIRRING

Equation (21) pertains to the type of experiment characterized by the function $\frac{u}{u'-u}L$, or its equivalent[5] $\theta u\frac{\delta\pi}{\delta\theta}$, denoted by the symbol $\beta$. The significance of this result has already been suggested during its development, and it is mentioned here again in order to emphasize the fact that this particular calorimetric process completes a coherent series of experiments from which several important thermodynamic properties may be found without using any other auxiliary data. This type of experiment consists in withdrawing saturated *liquid* from the calorimeter, maintaining equilibrium in the ideal case by adding the appropriate quantity of heat. Both in this type of experiment and in the one where vapor is withdrawn, the advantage of stirring is even greater than in the experiment where no fluid is withdrawn. Beside increasing the uniformity of temperature over the exterior surface of the calorimeter, and hastening attainment of equilibrium at the beginning and end of the experiment, a mode of circulation in which the liquid is compelled continually to flow in contact with the entire interior of the calorimeter wall, makes it possible to add the required heat at such a place and in such a way as to avoid undesirable disturbances of the internal pressure during the experiment. Greater perfection of the experiment in this respect reduces the uncertainty in the state of fluid withdrawn and thus conduces toward accuracy of the final result.

Experience with the latent heat calorimeter for ammonia showed that in the absence of stirring the process of evaporation and withdrawal of fluid was accompanied by sensible temperature differences within the system, due to the thermal resistance between the place where the heat was developed, and the free surface of the fluid where it was absorbed in the process of evaporation. While these departures from uniformity of temperature were not great enough to introduce any serious errors

[5] See equation (33).

into the results of those experiments, it is nevertheless well to consider how they may be avoided in any important analogous experiments. Vigorous circulation permits the transfer of heat to take place with less disturbance of temperature than would otherwise be possible. Moreover, when the heat supply just compensates for the rate of evaporation, less heat will be stored in the fluid as transitory superheat if the heat is developed nearer to the surface where it is to be absorbed. Such a closeness of thermal coupling will not only make the state of the evaporating surface more responsive to the rate of adding heat, but also lessen the temperature disturbances in the whole mass of fluid contents. In order to develop this idea better we shall next consider several instrumental refinements for improving control of the evaporation process.

## REFINEMENTS FOR CONTROLLING EVAPORATION

To be a little more specific, let us suppose that the liquid portion of the contents is vigorously circulated by a positive means such as a centrifugal or turbine pump at the bottom. Let the circulation in one direction follow the wall of the container, and return within a separating partition. Near the top at the interior space where the vapor will be confined, let a definite small fraction of the stream be diverted and caused to over-flow quietly in a broad cascade, so as to expose a large surface of the fluid and at the same time continually renew the surface. Let this shallow stream of liquid envelop and bathe the surface of an electric heater. To keep the whole surface of the evaporator wet it may be closely enveloped with fine wire gauze which will act as a wick. The less distance the heat has to travel before it is absorbed in evaporation, and the smaller the overflow the less heat will be swept out in the overflowing current as superheat. It is thus possible to avoid objectionable thermal disturbance of the main body of the liquid by suitably proportioning this part of the instrument. Another advantage to be gained by refining the design of the evaporator is the promotion of quiet evaporation, and avoidance of the spray which might otherwise be projected into the vapor, and affect its quality. The efficiency of the evaporator in this respect will set the upper limit to the rate at which vapor can be withdrawn without being wet.

## AUTOMATIC CONTROL OF HEAT ADDED

Automatic regulation of the heat supply is another point that invites consideration. If provision has been made for stirring and for

close thermal coupling between the heater and the evaporating surface, as outlined above, automatic regulation is simple to effect, and if successful, operates with the other two refinements to bring the experimental conditions nearer the ideal. A description follows of the manner in which experimental devices already demonstrated in practice might be adapted to effect this control. The vapor pressure at the free surface is the best variable for regulating the heat supply except perhaps at the lower temperatures where the sensitivity would be too low. Let the variation in pressure actuate an electric contact. The impulse, amplified if necessary by relays, may be made to vary the power in the heating circuit by a fixed amount, after the fashion of modern thermoregulators. The frequency of the cycle of power variation may be adjusted to allow sufficient time for periodic observations of the power at its two values. The duration of each period of constant power may be determined by ordinary chronographic methods, and the total energy transformed and added as heat found by summation.

To the reader who is familiar with the more special types of calorimetry, most of the principles of the proposed instrumental features will be recognized as old acquaintances. The experienced manipulator accustomed to precise quantitative control of fluids in respect of temperature, pressure, volume, mass and heat content, will perceive in the sketch an outline of the first and easiest step in an experimental project, i.e. the establishment of an ideal which may undergo considerable modification in the course of the more arduous work of developing the project.

In conclusion, it may be mentioned that a test of some of the foregoing proposals is in prospect at the Bureau of Standards in determining the thermal properties of water. It is hoped that this fact will not deter others from engaging in analogous work, for the danger of unprofitable duplication of effort along this line seems, at present, to be remote; and while it appears that systematic calorimetry of saturated fluids may be costly in the equipment and effort which are needed to cope with the incidental problems, we may in a final word recall the attractiveness of these problems and the wealth of useful data which will result from their successful solution.

BUREAU OF STANDARDS,
WASHINGTON, D. C.
FEBRUARY 10, 1923.

# A PHOTOMETRIC DISK VARIABLE AND DIRECTLY READABLE WHILE IN ROTATION, WITHOUT GEARS AND WITHOUT AUXILIARY ELECTRICAL OR OPTICAL DEVICE

By Enoch Karrer

The present contribution is a sequel to that[1] of recent date where it was shown that a variable sectored disk may be made distantly readable while in rotation by employing a Wheatstone branched circuit arrangement. Now, I wish to point out how such a disk may be constructed without any auxiliary devices, optical or electrical, and without the use of gears such as were used by Keuffel and very recently improved by Ives.[2]

The aperture in a variable sectored disk may be varied by moving the the disk itself (rotation around a horizontal axis or in azimuth when the sectors are arranged like louvres; and motion along or at right angles to the axis of the disk when the sectors themselves have adjusted or graduated angular dimensions); or it may be varied by moving opaque screens across the disk apertures. In the latter case the opaque screens are best made in the form of another disk which may slide over the other, and the problem then is to rotate two disks in synchronism, and yet allow them to be relatively displaceable. This may be done first by direct mechanical attachment to the same axis as in the Abney type and others patterned after it; secondly, by gears as in the disks of Keuffel and Ives and so nicely illustrated by the rear wheels of an automobile; and thirdly, by electromagnetic coupling of the two disks mounted upon separate axes as illustrated by the disk about to be described.

One means of electromagnetically maintaining two disks in synchronism is to mount the disks upon the axes of two impulse motors excited by current that is interrupted by the same tuning fork, for instance. A somewhat simpler method was employed to make the preliminary observations to be noted here. Two small synchronous motors as are used in oscillographs were appropriated. Upon one end of each axis

[1] J. O. S. A. & R. S. I., 7, p. 893; 1923. The present paper is a part of the one referred to there ' in which certain other forms and new uses of the sectored disk" were to be described. On account of some interruption of work only this portion which has more uniqueness than the other is presentable at this time.

[2] J. O. S. A. & R. S. I., 7, p. 683, 1923.

was mounted a small aluminum disk whose planes could be placed parallel and very close to each other. This is made clear by Fig. 1 where a diagrammatic sketch is given suggestive of a sectored disk constructed along these lines. The two synchronous motors A, B, operate on a 110 volt, 60 cycle, line. They have 4 field coils $s, S$; and 4 rotor magnets $r, R$. Upon their axes are mounted the two disks $d, D$. The stator of one of the motors $B$ is mounted in bearings so that it may easily be turned through any angle which is read from a graduated

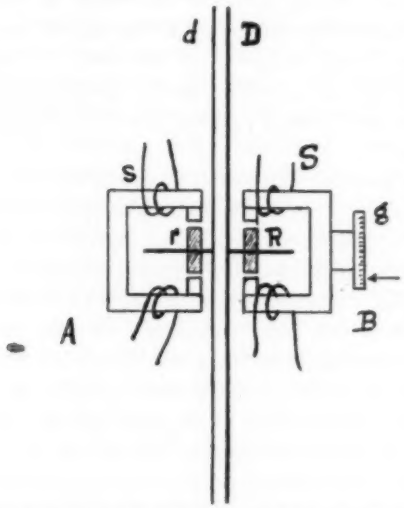


FIG. 1. *A variable photometric disk made of two disks each mounted upon the axis of a synchronous motor.*

cylinder or wheel $g$. The phase difference, in other words, is indicated by the scale $g$. The relative aperture through the two disks running in synchronism depends upon this phase difference so that the scale $g$ directly indicates the relative depletion factor of the disk. The phase may be altered by other means than by the actual turning of the field, for it depends upon the electrical constants of the field circuit, and these may be changed by inserting more or taking out capacity for example. In the latter case the disk becomes at the same time adjustable and readable electrically at any distance. It may be of interest to point out that the disks need not necessarily be juxtaposed as indicated above, but may be even widely separated in an optical

system,—due attention being given to the size of slits and elimination of parallax.

The two small synchronous motors with which my preliminary observations were made seemed to perform well, but no test for accuracy or constancy over extended periods of operation were made.

WIRE DIVISION,
NATIONAL LAMP WORKS OF GENERAL ELECTRIC CO.
CLEVELAND, OHIO.

**Ionizing Potentials of Helium and Some Multiatomic Gases.**—Photoelectrons excited from nickel by ultraviolet light were used instead of electrons from a hot filament, to avoid the chemical actions likely to occur between hot metal and the gases used. The electrons were accelerated into a cup-shaped chamber faced with a metal gauze into which a narrow wire was thrust from below to serve as collecting electrode for positive ions. Although the potential of the wire was only 6 to 8 volts below that of the chamber, while the latter was at times as much as 50 volts above that of the filament, the author seems to have had no difficulty in detecting the onset of ionization and distinguishing it from radiation. Mercury vapor was mixed with helium, and the difference between the ionizing potentials determined as 14.1 volts, yielding *24.5 volts* for the ionizing potential of helium. This value agrees with the convergence frequency of the helium series discovered in the far ultra violet by Lyman, and supports Franck's action in correcting his and Knipping's original value of 25.3 to 24.6 (ZS. f. Phys. *11*, pp. 155-160; 1922). Helium was then mixed with the other gases studied, and the differences in ionizing-potential measured; yielding the following values: Nitrogen 16.3, oxygen 12.5, HCl 13.8, HBr 13.2, HI 12.8, water vapor 13.2, ammonia 11.1. The curves of current-versus-voltage reproduced in the article display long gradual bends connecting one rectilinear portion with another; the "ionizing potential" is located by extending the rectilinear portions to intersection. [C. A. Mackay (Princeton) Phil. Mag. *46*, pp. 828-835; 1923.]

K. K. DARROW

**Change of Wave Length Accompanying X-ray Scattering, Deduced from Absorption Measurement.**—In these experiments a beam of X-rays from a Coolidge-tube was played upon a target, and the scattered beam received in an ionization chamber. By interposing an absorbing screen first in the path of the primary beam and then in the path of the scattered beam, and measuring the intensity of the scattered beam in each case, the difference between the absorbing power of the screen for the two beams was determined, and then the difference in wave length was calculated from the preassumed absorption coefficient versus wave length relations for the screen. Fluctuations in the

intensity of the source are compensated by receiving a direct beam from it in a second ionization chamber connected in series—opposing with the first one. The data relate to primary X-rays of wave lengths ranging from .024 to .90 A; to the substances paraffin, paper, graphite, Al, Cu, Pb as scatterers; and to scattering angles ranging between 30° and 135°. Generally speaking, the scattered wave length increases steadily with angle of scattering, and the increase approaches more nearly to the theoretical value $\delta\lambda = h(1-\cos\theta)/mc$, the lighter the scattering atoms and the higher the primary frequency. At wave length 0.15 A the agreement for carbon and paraffin is good, while the change in wave length for scattering by lead is only about half the value which the formula gives. This result may indicate that electrons of the heavier atoms do not recoil from an encounter with a quantum, so that the quantum rebounds as from an immobile mass without loss of energy or frequency; this might be because the electrons are more tightly bound to the nucleus, or because they are so close together that the quantum enters into collision with a large number of them at once. Compton suggests that the reason why the radiations from the sun's limb are in general of slightly greater wave length than those from the center of the disc is that the former radiations are scattered by the free electrons in the solar atmosphere.—[A. H. Compton, (Washington University); Phil. Mag. *46*, pp. 897–911; 1923.]

K. K. DARROW

**Polarized Phosphorescence.**—A solution of eosine in gelatine, illuminated by two beams of light falling on adjacent patches of it and polarized at right angles to one another, shows when examined with a phosphoroscope strong polarization of the phosphorescence-light from the two patches; the light from each is partially polarized, in the same plane as the exciting light; the difference in the brightnesses of the two patches, when viewed through a Nicol prism, is great enough to be distinctly visible in photographs. Examined quantitatively with a Savart plate, the light is found to be about 21% polarized. This light is emitted during a period of 1/800 second, beginning 1/400 second after the end of an illumination-period itself 1/800 second long; shortening the periods in question in the ratio 1 : 3 did not alter the degree of polarization; the fluorescence-light of eosin, (doubtless much mingled with phosphorescence-light) is itself 22% polarized, according to Weigert. A boric-acid phosphor, however, displayed no polarization either of the fluorescence or of the phosphorescence-light. Note that the phosphorescence-spectrum of the eosin in gelatine is identical with the fluorescence-spectrum of eosin in water, while no such identity exists in the case of the boric acid phosphor.—[A. Carrelli & P. Pringsheim, Berlin; ZS. f. Phys. *17*, pp. 287–291; 1923.]

K. K. DARROW

# A SOURCE OF CONSTANT FREQUENCY OSCILLATIONS

By Ross Gunn

Very often the laboratory worker has urgent need for an electrical oscillator whose frequency may be varied over a rather wide range but which will remain at the desired frequency when once adjusted. At present there seems to be no satisfactory device that will fulfill this need, for the tube driven forks are unsatisfactory at the best.

In all the ordinary vacuum tube oscillating circuits commonly used the frequency of the generated oscillations varies rapidly as the filament current and anode potential change. Except when extraordinary care is used in maintaining these factors constant the frequency of oscillation will vary enough to make the usual methods hopeless. The writer was called upon to devise a system that would maintain the frequency virtually constant under the rather trying conditions encountered in the field. The method of using two tubes as shown below was the simplest solution of the problem and has been found to be exceptionally satisfactory in practice.

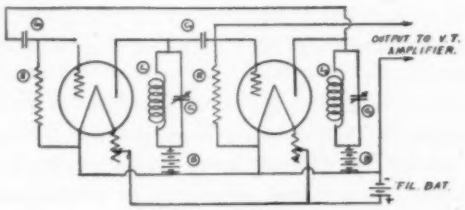


*Diagram of connections*

The diagram shows the general method used. In this particular case tuned impedance type of coupling was used, although there are many advantages in using tuned (and iron free) transformers or properly designed filter sections in place of the tuned impedances $(LC)_1$ and $(LC)_2$. Some care must be used in tuning even at audible frequencies, otherwise the oscillations are feeble and the frequency will vary noticeably with changing plate voltage and filament current.

An examination of the diagram will show that the tubes stand in exactly the same electrical relation to one another. Thus it is apparent that if a given voltage be impressed on the grid of one tube the effect of this voltage will be passed on to the next one which will repeat the operation and return to the original grid the same impulse amplified

and approximately in phase with it. Obviously then, the system will oscillate and any impulse applied to the grid of either tube is passed through the system again and again and in this manner all frequencies are rapidly attenuated except the one for which the coupling unit is designed. By properly designing the coupling units (tuned impedance, tuned transformer) it is easy to build an oscillator which will oscillate at practically one frequency, or if oscillations are suppressed the arrangement may be used as a very selective filter. It should be observed that an even number of tubes are necessary if the simple impedance type of coupling is used to insure the proper phase relations on the successive grids.

The value of the constants of the circuits depends on the frequency to be used. $L$ and $C$ should be of such a value as to give the desired frequency (i.e. $f=\frac{1}{2\pi\sqrt{LC}}$ approximately) and should be so proportioned that the tuning is fairly sharp (i.e. $\frac{1}{R}\sqrt{\frac{L}{C}}$ should be made as large as possible). The value of $C_g$ should be such that its impedance at the desired frequency is small compared to the input impedance of the tube used. The grid leaks $R$ will depend on the tube and must be determined by experiment. In some cases chokes and biasing batteries are used to the best advantage.

If more than five or ten percent of the rated power of the tubes is to be used it is advisable that the output leads be connected to an amplifier and the load carried by the amplifier. In this way, for example, a small synchronous motor might be driven at a constant speed—the speed being determined by the frequency of the oscillator.

On a certain oscillator similar to the one described below and working at 1000 cycles it was found by beat methods that the frequency variation was less than one-tenth of one percent for a plate voltage change of 50%, and a change of three-tenths percent for a 43% change in filament current. It would then appear that any ordinary variations in the power supply to the tubes would be negligible.

In the course of development it was necessary to make an oscillator for low frequency (1000 cycles). The values used in this oscillator will be given in order to illustrate the method of procedure in design and give exact details for a particular case. The inductances $L_1$ and $L_2$ were similar and were made by winding a slot 7/8″ by 7/8″ cut in a 3½ circular block full of No. 27 B & S Enameled wire. This gave an approximate inductance of 230 millihenries. The condensers shunted

across these inductances were 0.10 microfarad with a variable portion which could increase it to 0.12 microfarad by small steps. The grid condensers $C_g$ were 0.25 microfarad which had an impedance at 1000 cycles of approximately 650 ohms. At this low frequency it was found desirable to substitute for the grid resistances a biasing battery and a choke. The tubes used were the Western Electric coated filament "J" or V. T. l.s. Using these tubes with an iron core choke of approximately 0.80 henry and 600 ohms resistance it was found that a negative bias on the grid of 4½ volts was the best. A plate voltage of 45 was used with these tubes.

The writer hopes that the above description will aid those who are interested in building such a device and he feels sure they will be rewarded for their efforts if proper care is taken to tune the separate sections to the same natural frequency. The oscillator described above was developed while the writer was employed as Radio Engineer by the Engineering Division of the United States Air Service.

SLOANE LABORATORY,
YALE UNIVERSITY,
NEW HAVEN, CONN.

**Science Remaking the World.** Edited by Otis W. Caldwell, Ph.D., Professor of Education, Columbia University, and Edwin E. Slosson, Ph.D., Editor of "Science Service." xii+292 pages. Doubleday, Page and Company, New York. $2.50.

The present volume puts in book form a series of lectures, given by various scientists during the summer of 1922 at Teachers College, Columbia University. The purpose of the course was to give students of all subjects an understanding of the achievements of modern science, in its various branches, and its influence on modern thought and on present day social and industrial relations. Because of the audience which the lectures were intended to reach they were presented in popular, though accurately scientific, style, entirely devoid of unnecessary technical terms. A very refreshing mixture of pure and applied science runs throughout the entire volume. And, more important, the several lectures have introduced here and there interesting bits of scientific history and biography. For, as the Editors state, "it is important for the public to understand that scientific progress is not a mere series of lucky accidents,—but a long and toilsome process of investigation—on the part of many workers." It is not unpatriotic to compare, as regards its value to human society, the work of Abraham Lincoln with that of Louis Pasteur. Yet how many know anything of

the personal life of the latter? Read the chapter "Louis Pasteur, and Lengthened Human Life," and then reflect on the human interest in science as well as in statesmanship.

To attempt to give a summary of the book is of course impossible since each of the sixteen lectures is itself a summary of a vast field. A great variety of subjects is covered—from "Electrons and How We Use Them" to "The Modern Potato Problem." Among the other subjects discussed, each in a lecture, are Gasolene, Coal-Tar, Influenza, Tuberculosis, Public Health, Modern Botanical Gardens, Evolution, Applied Entomology, Insect Sociology, Forests and Clouds, Chemistry and Food, and Vitamins. Following each lecture is a list of references for supplementary reading. The several lecturers and the Editors have done both Science and the public a valuable service in making these lectures available in book form.

F. K. RICHTMYER

**Elementary Optics and Applications to Fire Control Instruments.** Prepared under the direction of the Chief of Ordnance, May, 1921. Government Printing Office, 1922. Pp. 106. 95 Figures.

The unnamed author of this little treatise on one branch of applied optics is to be congratulated on assembling such a quantity of useful information in such concise, readable form. The book is an outline of elementary geometrical optics followed by a more extended discussion of the telescopic system and a somewhat detailed review of the major characteristics of numerous modern fire control instruments. Principles of design, limits of sensitiveness and errors of adjustment are properly emphasized. The book was prepared for use as a textbook in Army training schools and as a reference handbook by officers and men using optical fire control apparatus.

Despite and because of the excellence of the material presented, one cannot but wish that it had been expanded about three-fold in each section, thus strengthening and clarifying the general portions on lenses and adding interesting detail to the treatment of special instruments. A 300 or 400 page treatise on the general subject of the optical instruments used in war, following Col. F. E. Wright's treatise on Optical Glass should be very valuable indeed.

P. G. NUTTING

# A SILVER CHLORIDE BATTERY FOR POTENTIAL PURPOSES

By Henry A. Erikson

A low current battery giving about 100 volts is of such convenience in a laboratory where quadrant and string electrometers are used that a special design for this purpose has been found justifiable. Batteries constructed as described below have been in use in this laboratory for a number of years and have given satisfaction from the standpoint of permanence and convenience.

The cell is of the silver chloride type. The electrodes are of the form shown in Fig. 1. B is a silver wire No. 16 S.W.G. and 10 cm long, extending from the upper end of the zinc electrode *A* to the lower end

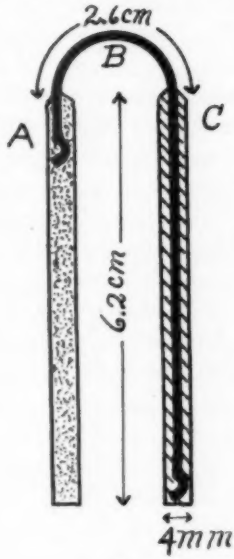


Fig. 1

of the silver chloride electrode *C*. The zinc electrode *A* is cast in an iron mould which has a neck of same diameter as the silver wire. The straight silver wire is laid in the neck of the mould so as to project into the mould one cm as shown at *A* Fig. 1. The two halves of the mould are clamped together and the molten zinc poured into the

open end opposite to *A*. Ten or more of these moulds may be in the same piece of iron and all poured at the same time. Before pouring, the mould should be heated nearly to the temperature of the molten zinc.

The silver chloride electrode *C* is then cast about the other end of the silver wire in the same mould as used for the zinc electrode. The wire in the case of this electrode extends the whole length of the mould as shown in Fig. 1. It is desirable to bend the wire near the ends as indicated. The mould must be heated to nearly the temperature of the silver chloride before pouring. The silver wire being straight while the electrodes are cast about it may now be bent at *B* into a yoke as shown.

Glass specimen tubes 1.8 cm internal diameter and 8 cm deep are used as cell jars. These are placed in rows of 10 and are 0.5 cm apart. The electrodes form yokes between the jars. The jars are placed in holes bored in a wooden base and set in paraffin. A base $30 \times 29$ cms will allow 10 rows of 10 cells.

The tray is placed inside a wooden case of $30.5 \times 29 \times 10$ cm inside dimensions, the front of which is provided with hinges.

The leads from the battery terminate in plugs which may be inserted in sockets placed in the sides of the case near the front.

The liquid used is a 5% solution of zinc chloride to which a drop or two of hydrochloric acid has been added for clarifying. The solution in each cell is covered with .5 cm of paraffin oil.

The silver chloride is readily prepared by dissolving silver nitrate in water and precipitating with hydrochloric acid. After it has been dried it is melted in a porcelain ladle and poured directly into the heated mould.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA.
JULY 6, 1923.

# THE VARIATION WITH TEMPERATURE OF THE PHOTOELECTRIC EFFECT IN POTASSIUM PHOTOELECTRIC CELLS

By Herbert E. Ives

ABSTRACT

*Variation of Photoelectric Current with Temperature.* The photoelectric current from pure potassium, in highly exhausted cells, is found, contrary to previous belief, to vary with the temperature, and in the sense of the temperature change. The temperature range investigated was from room temperature to the temperature of liquid air; the variation of the photoelectric current with temperature is negligible above 0°C but becomes greater the lower the temperature. The change in photoelectric current is greater the lower the frequency of the exciting radiation, and occurs in both the normal and selective photoelectric effects.

*Variation of Surface Work Function with Temperature.* The variation of photoelectric current with temperature is shown to be in harmony with the supposition that the work function of the surface is altered. Such an alteration of the work function is shown experimentally by the occurrence of a bodily shift along the voltage axis of the voltage-current curve of a photo-sensitive cathode when the potassium, which is changed in temperature, is the anode. It is further checked by the change in the long wave-limit of photoelectric emission of the surface whose temperature is varied. On cooling potassium from +20° to −180°C its work function is increased by about 1/5 volt.

## 1. Introduction

The photoelectric cell is coming into increasing use, both in connection with the measurement of light and in connection with the utilization of light in the arts. Full information on its characteristics is therefore of increasing practical value. At the same time the importance of the photoelectric effect in relation to the theory of radiation, particularly of the interaction of radiant energy and matter, warrants its close study. The work here reported is part of a series of investigations on the theory and applications of the photoelectric cell, and deals with the influence on the cell of the variable *temperature*.

It is commonly held that the photoelectric effect is unaffected by varying the temperature of the electron emitting surface. This belief is based upon a large number of experimental researches. Passing over certain early investigations, which were conducted under experimental conditions which would not now be considered sufficiently good to form the bases for valid conclusions, the chief work upon this subject is that of Lienhop,[1] Ladenburg,[2] Millikan and Winchester,[3]

[1] Lienhop, Ann. der. Physik, *21*, p. 281; 1906.
[2] Ladenburg, Verh. d. d. Phys. Ges., *9*, p. 165; 1907.
[3] Millikan and Winchester, Phil. Mag., *14*, p. 188; 1907.

Varley and Unwin,[4] and Dember.[5] Certain of these investigations dealt primarily with the initial velocities of emission of the photoelectrons and others with the magnitude of the photoelectric current. The experiments of Lienhop upon the initial velocities were made upon soot and platinum black, and were performed over the range from room temperature down to the temperature of liquid air. Ladenburg, using platinum, gold and iridium, investigated the photoelectric effect from room temperature up to 860°. Neither of these investigators found any dependence of initial velocities upon temperature. Millikan and Winchester studied a large number of the common metals over the temperature range from 15° to 125° C and found no variation of the photoelectric current over this range. Varley and Unwin working with platinum over the temperature range 60 to 350° C found the photoelectric current unchanged. Dember, who alone of the more recent investigators studied the alkali metals, made observations upon sodium and potassium from room temperature up to the melting points of these elements, 97° and 62.5° respectively. He found no change in the photoelectric current.

In view of the results described in the present paper, it is of interest to note that while the group of experiments just described covers a temperature range from −180° C to +800° C, this entire range is not covered with all of the photoelectric materials investigated. There is in fact a rather noteworthy hiatus in that the alkali metals have not been studied at temperatures lower than 25° C. As the present paper shows, it is in just this field of experimentation, namely, the alkali metals at temperatures running down from room temperature to that of liquid air, that variations of the photoelectric phenomena with temperature occur.

## 2. PRELIMINARY OBSERVATIONS

The observations which led to the present study were made in the course of an investigation of another kind of photoelectric phenomenon which has been described elsewhere.[6] In that investigation it was found that the rate of response of oxide coated filaments to excitation by light varied greatly with temperature. This suggested a check experiment on one of the ordinary photoelectric metals, in order to verify the common belief that the photoelectric effect with pure metals

[4] Varley and Unwin, Proc. Roy. Soc. Edin. *27*, p. 117; 1907.
[5] Dember, Ann. der Physik, *23*, p. 957; 1907.
[6] Arnold and Ives, Proc. Nat. Acad. Sci., *7*, p. 323; 1921.

is instantaneous at all temperatures. The experiment when performed with a potassium photoelectric cell indicated no difference in quickness of response at room temperature and liquid air temperature. However, a difference in the size of the photoelectric current was noticed. This change in the size of the photoelectric current was later made the subject of a separate study, the outcome of which is the present paper.

### (a) TYPES OF PHOTOELECTRIC CELLS USED

During the course of the work between 40 and 50 different photoelectric cells were used; several were the identical cells used in an earlier investigation dealing with the illumination-current relationship,[7] the majority were constructed for the present study. Many of the cells were of quite special designs which will be described in the appropriate place. Fig. 1 shows a type of cell which conforms in its essentials to the first cells experimented with, and a description of it will serve to disclose the essential features of a cell for showing the effects of temperature on the photoelectric effect. The cell consists of a bulb whose walls are covered, except for a small window, with potassium, which forms the cathode. The anode consists of a loop of wire at the end of a fairly long glass stem. The potassium on the bulb wall is in contact with a platinum wire which leads out from a separate tube parallel with the main stem. A charcoal tube is carried off to one side (to the rear in the figure). The whole cell is constructed so that it may be immersed in a Dewar flask. Special flasks were constructed for the work, provided with a clear window through which (and a layer of liquid air or other cooling or heating liquid) the interior of the cell might be illuminated.

The process of exhausting and filling used throughout the work was substantially as follows: The cells, of pyrex glass, were made up with a series of three or more bulbs attached, for the purpose of introducing the potassium by distillation. This whole system was enclosed in an oven held at 400° C and exhausted for several hours by a mercury aspirator pump working through a liquid air trap. The potassium, in the form of a slug, broken off a pyrex tube into which it had been previously distilled to free it of gas, was then introduced into the distilling system, and, at the same time, a charcoal tube was attached to the cell. The whole system was exhausted, the potassium was melted down into the first bulb, and the cell proper was again placed in the oven. The potassium was then slowly distilled by an oven maintained

[7] Ives, Dushman and Karrer, Astrophys. Journ., p. 9, Jan. 1916.

at 400° to 500° C into the bulb nearest the cell, while the charcoal tube was repeatedly roasted out with a flame until no more gas was

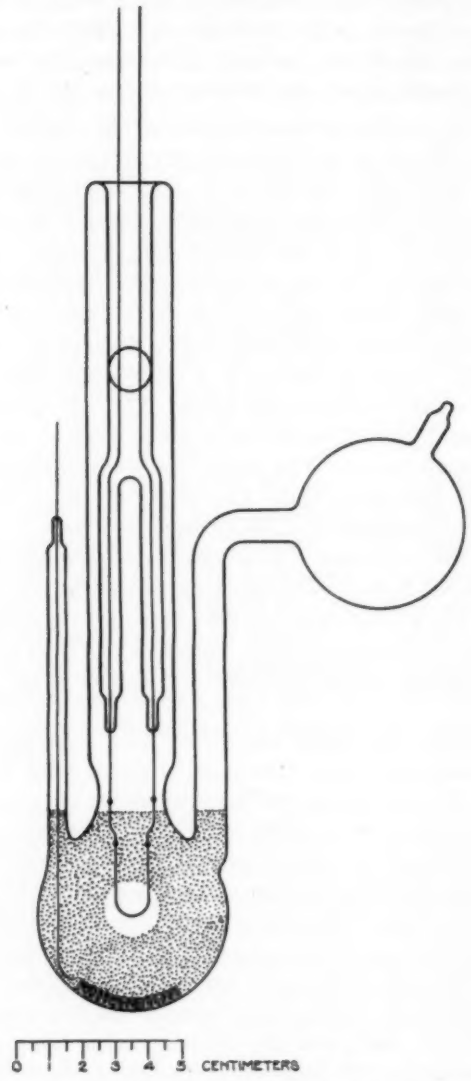


FIG. 1. *Type of photoelectric cell suitable for showing temperature effects.*

given out on raising the tube to just below the softening point. The train of distilling bulbs, excepting the one nearest the cell, was then sealed off, the oven was removed and the potassium distilled into the cell and condensed on its walls by the application of ice water, the charcoal tube being meanwhile held at 400° C by an oven. Then, after further pumping, the cell was sealed off from the pump and the oven removed from the charcoal tube. The pressures on the pump system, when the cell was sealed off, were below $10^{-5}$ mm of mercury, as read by an ionization manometer. Except where otherwise noted, the cells were studied with the charcoal tube in liquid air. The baking and slow distillation processes gone through are believed to make the cells as free from gas as it is possible for present-day high vacuum technique to assure.

(b) EFFECT OF TEMPERATURE ON THE PHOTOELECTRIC CURRENT

When the photoelectric current in cells of this design is measured at room temperature (the Dewar flask filled with water or paraffin oil) and then at the temperature of liquid air, it is found that the photoelectric current is diminished by the decrease in temperature. The change of photoelectric current with temperature is reversible, for upon warming up to room temperature, the current assumes very nearly, although usually not exactly, its original value. There does not appear to be any progressive fatigue in the temperature effect, although the first time the potassium is cooled the effect is apt to be larger than it is in subsequent coolings.

This effect has been checked many times with a great variety of cells, and occurs not only with potassium but, as a few experiments have shown, with sodium. The amount of the decrease of photoelectric current with decrease of temperature depends markedly upon the wave-length of the exciting light. Typical results are shown in the voltage-current curves of Fig. 2, where the photoelectric currents (read on a sensitive d'Arsonval galvanometer) are shown for yellow and blue light (tungsten lamp and colored glasses) for room and liquid air temperatures. The change in the photoelectric current for blue light for this temperature range is approximately 20%, for yellow light 45%. (At very low voltages the effect of the liquid air is to increase the photoelectric current, a point which will be explained later.) In general, the longer the wave-length, the larger the effect of temperature. If deep orange or red light is used the effect of immersing the cell in liquid air may be a practical inhibition of the photoelectric

current. Figure 3 shows the variation of photoelectric current (at a voltage high enough to give approximate saturation) for several colors of light over the temperature range from 50° down to −180° as given by measurements at 50°, 0°, −80° (carbon dioxide and ether) and −180° (liquid air). The results have been plotted in terms of equal values at 0°. It will be noted from this figure that the variation of the photoelectric current with temperature is apparently continuous, although the rate of change is much more rapid toward lower tempera-

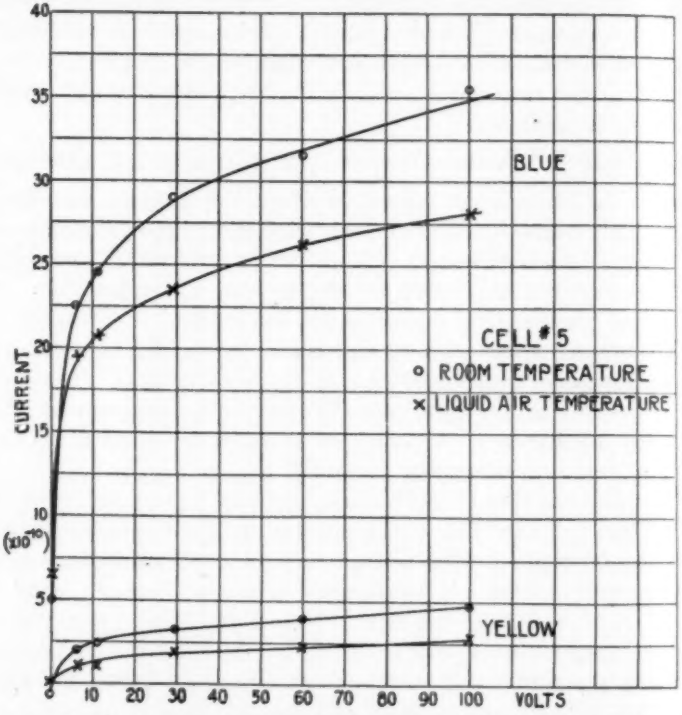


FIG. 2. *Photoelectric currents at room and liquid air temperatures for yellow and blue light.*

tures. The rate of decrease is more rapid for the long than the short wave-lengths. Furthermore it will be seen that the temperature range investigated by Dember (25° to 50°) is one in which the variation with temperature which is here noted is entirely negligible.

### (c) TESTS TO ELIMINATE THE POSSIBILITY OF GAS EFFECTS

As described above, the method of evacuating the cells and the precautions taken in the distillation of the potassium are thought to

eliminate the possibility that these cells contain any appreciable amount of gas. Nevertheless the experiments just described suggest to everyone that the apparent variation of photoelectric current is due to a variation in the vacuum in the cells. It is, of course, well known that sodium-potassium alloy will absorb large quantities of gas and it is very likely that potassium when cooled to liquid air temperature will act somewhat like charcoal as an absorber of gas. The possibility of the effects above described and those which are described further on in the paper being due to a condensation of residual gas upon the

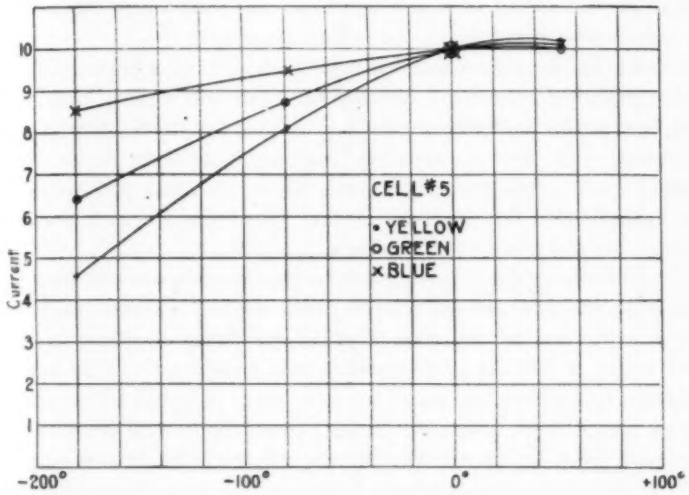


FIG. 3. *Variation of photoelectric current with temperature for yellow, green and blue light.*

surface of the alkali metal cannot be excluded and may indeed be the explanation of everything found. However, a number of experiments which will now be described are considered to pretty well eliminate the possibility of any gross change in the gas pressure in the cell being responsible for the effects, and also to render unlikely the explanation just suggested in terms of gas condensation on the metal surface.

First of all, a cycle of experiments was tried, with and without the charcoal tube being immersed in liquid air. These showed (1) that with the potassium at room temperature its photoelectric current was not altered in magnitude by the cooling of the charcoal; (2) that

the decrease of current on cooling the potassium with liquid air occurred irrespective of whether the charcoal was cooled or not.

A second experiment consisted in shaking down a large quantity of the charcoal from the charcoal side tube into a position beneath the potassium, which was collected into a large globule on the side of the cell. This charcoal was first thoroughly cooled in liquid air, then the liquid air was moved up to surround the potassium. The intention in this experiment was to absorb all free gas in the neighborhood of the potassium by means of the charcoal before the potassium itself was cooled. No change in the photoelectric effect from the globule of potassium was found until the liquid air was raised into contact with the glass wall against which the potassium lay.

A third experiment consisted in constructing a cell with an additional bulb containing potassium, opening into the first bulb. This second bulb was placed in liquid air for a long time before the first one was immersed, with the idea that the auxiliary potassium surface would condense any gases present, if any, which the charcoal would not. The behaviour of the potassium in the first bulb upon its immersion in liquid air was unaffected by this procedure.

An opportunity for an even more conclusive experiment along the same lines was afforded later in the work when a cell was constructed with a hollow central electrode (Fig. 10), on which, as well as upon the outer walls, a coating of potassium was condensed. This cell was immersed and allowed to stand for four hours in liquid air; at the end of this time the photoelectric current from the central electrode was measured, then liquid air was introduced into the central electrode and the current again measured. It showed the same decrease in value noted in other types of cells. Since in this cell the potassium surface in the walls had about 50 times the area of that on the central electrode, it would seem likely that any gas present capable of condensation on cooled potassium would have been completely condensed on the walls before the central electrode was cooled.

These experiments, which were amply supported by similar experiments performed incidentally during the course of the work, sufficed to indicate that the depression of the photoelectric current upon decrease of temperature was a real effect of the alkali metal surface, not dependent upon the pressure of such residual gas as might be present. It also appears unlikely that the effect can be ascribed to condensation of gas on the potassium surface.

### 3. TENTATIVE EXPLANATION OF TEMPERATURE EFFECT AS A CHANGE OF THE WORK FUNCTION

While a variation of the photoelectric current with temperature is in conflict with all previous work on the subject, and with the theoretical speculations on the nature of the photoelectric effect which appear to render such an independence of temperature reasonable, it was early recognized in the present investigation that a possible explanation of the results existed which would not do great violence to prevalent ideas of photoelectricity. This explanation is that the effect of variation of

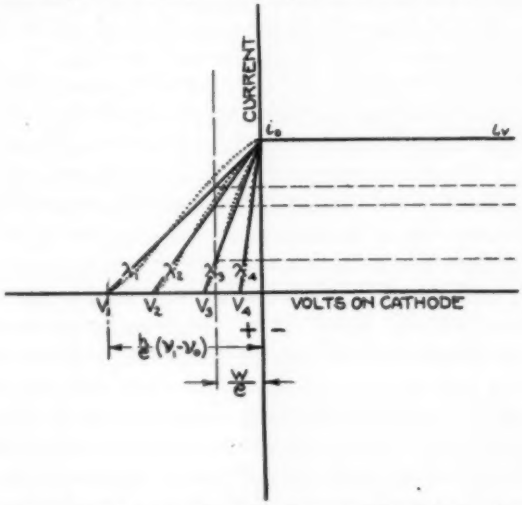


FIG. 4. *Voltage-current relations in an ideal photoelectric cell.*

temperature of the emitting surface is to *alter the work function of the surface*. How a variation of the surface work function could result in effects of the kind described in the last section can be made clear by examination of Fig. 4.

In this figure the axis of abscissae shows voltages applied to the photoelectric surface, the ordinates are photoelectric currents. $V_1$, $V_2$, $V_3$, and $V_4$ are the stopping potentials, or the positive potentials which must be applied to prevent electrons leaving the surface when illuminated by light of wave-lengths $\lambda_1$, $\lambda_2$, $\lambda_3$, $\lambda_4$. The $V$'s are related to the $\lambda$'s by the well known relation $V = \frac{h}{e}(\nu - \nu_0)$ when $\nu$ is the frequency corresponding to $\lambda$ and $\nu_0$ is the frequency corresponding to the long

wave limit of photoelectric action. It is assumed that the anode is of the same material as the cathode so that the photoelectric current is saturated at zero volts, and for convenience of discussion the saturation currents are represented as equal for all wave-lengths ($i_0$, $i_s$). The actual relation between voltage and current, below the saturation point, as found by experiment, is represented by the dotted lines of flattened S shapes between $V_1$ etc. and $i_0$.

If now, the work function of the emitting surface is changed, as by the substitution of another material, experiment shows that the intercepts of the voltage current curves with the voltage axis, ($V_1$, $V_2$, $V_3$, $V_4$) are not changed, but the saturation voltage is moved by an amount $w/e$, where $w$ is the change in work function. If this change is an increase, the saturation point is moved in the positive direction on the diagram, as shown by the dashed vertical line. When such a change in work function takes place it is evident from inspection of the diagram that certain wave-lengths, e.g. $\lambda_4$, can no longer cause the emission of electrons. It is a further experimental fact that as the cathode material becomes more electronegative (increase of work function) the photoelectric current for a given excitation decreases. The exact relationship between the various factors concerned is not known; the simplest assumption to make (O. W. Richardson)[8] is that the only significant difference between different materials is in the value of the work function, and that the change in saturation current is proportional to the change in (effective) saturation voltage, that is, that in Fig. 4, the saturation point "slides down" the straight line from $i_0$ to $V$. Inspection of the figure shows at once that if this is the nature of the change caused by a change in the work function, it will be of increasing magnitude the greater the wave-length, as indicated by the horizontal dashed lines.

If the saturation points move along the straight lines indicated as the work function is altered, then it is probable that the voltage current curves below the saturation point assume the characteristic S shapes for each position, so that two curves corresponding to two work functions will not coincide. Actually, however, the curves are sufficiently flat so that to a high degree of approximation we may picture the effect of an increase in work function, according to the assumption made, as primarily a decrease in the saturation current, leaving the unsaturated portion of the voltage-current curve virtually unchanged below the new saturation point.

[8] Richardson, Phil. Mag., *24*, p. 570; 1912.

The behavior of the photoelectric voltage-current relation, just outlined on the basis of a substitution of one cathode material for another, we shall suppose to hold where, instead of introducing a new electrode, we change the work function of the cathode by changing its temperature. The greater part of the work done in this investigation was undertaken to establish definitely whether the actual phenomena were in all respects in agreement with this interpretation of the influence of temperature on the photoelectric effect.

## 4. INCREASE OF WORK FUNCTION ON COOLING DEMONSTRATED BY THE ALTERED VOLTAGE—PHOTOELECTRIC CURRENT CURVE OF THE COOLED ELECTRODE

Probably the most obvious test of the theory advanced is to obtain voltage current curves of the sort shown diagrammatically in Fig. 4, and ascertain whether the decrease in photoelectric current is accompanied by the postulated shift in the saturation point. Actually it has been found that the experimental difficulties in the way of getting unambiguous curves of this sort are excessive, and a quite different line of attack, described in the next section, yields much more satisfactory proof of the suspected change in work function. Nevertheless the results obtained in endeavoring to get satisfactory voltage-current curves are important contributions to the final conclusion, and have several features of interest.

In order to obtain the type of curve desired it is necessary that the alkali metal cathode be of as small dimensions as possible and that it be located in the center of a large, completely enclosing, photoelectrically insensitive anode. Cells of this general type, in which the effects of electron reflection are minimized, were first made by Richardson and Compton.[9] The necessity, in the present case, of providing means for cooling the central electrode by the introduction of liquid air, presents constructional problems of some difficulty; these were, however, overcome by the use of a double-walled glass tube, the outer wall of which was perforated with an opening opposite the window in the large copper cylinder which served as anode. The potassium was flowed into the space between the two walls of the glass tube, and liquid air, when required, into the inner tube (Fig. 5).

The experimental results obtained with cells of this type were quite disappointing, for two reasons. The first disappointment was in the

[9] Richardson and Compton, Phil. Mag., *24*, p. 575; 1912.

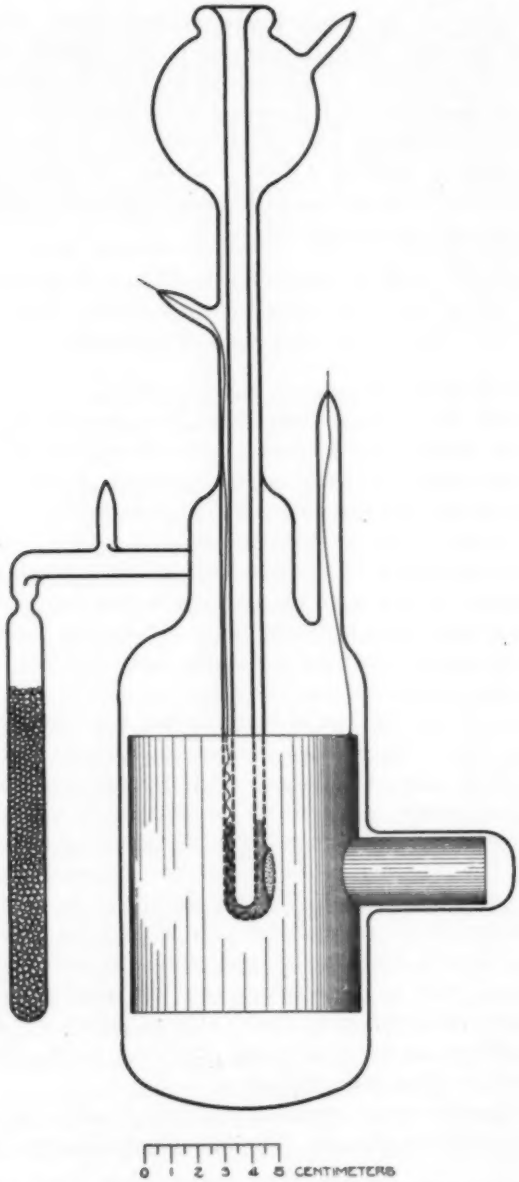


FIG. 5. *Special type of cell, containing central potassium electrode arranged for cooling with liquid air.*

discovery that it was quite impossible to prevent the anode from becoming highly photoelectric almost immediately, due to the condensation upon it at room temperatures of potassium vapor. As a consequence, the voltage-current curve does not come to an end at zero current, but extends to large negative values (Fig. 6); a study of the behavior of the stopping voltage was therefore made impossible. The properties of these quickly formed alkali metal films will be discussed in a separate paper. Suffice it to say that with really pure potassium in a high vacuum, it is impossible to prevent their formation within a very few minutes. The second disappointment was ex-

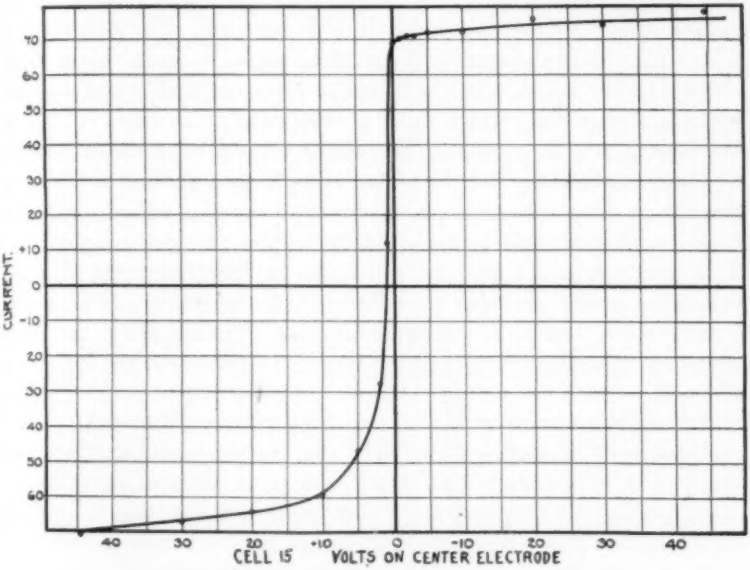


FIG. 6. *Voltage-current curve of central electrode cell.*

perienced when the experiment was tried of pouring liquid air into the inner tube to cool the potassium. Instead of the expected decrease of the photoelectric current, a very great *increase* was found, the increase amounting to three or four-fold.

This increase of photoelectric current upon cooling the centrally placed emitting electrode is complementary in almost every respect to the decrease previously found. The relative increase is thus greater for long wave radiation than for short; the cooled surface exhibits sensitiveness for long wave energy to which it previously appeared

insensitive. It is, like the decrease, reversible, upon return to room temperature. It is, however, a much slower process, taking as much as an hour to reach its full value where the previously noted temperature effect is completed as soon as the temperature reaches equilibrium. Because of its magnitude it is a much more striking phenomenon than the decrease on cooling first observed. Nevertheless, if the explanation given below is correct, it is a less significant and important effect than the much smaller decrease of emission caused by cooling under other experimental conditions.

A great deal of time was spent in searching for the explanation of this increased emission. It was ultimately traced very definitely to the *condensation of potassium vapor* on the electrode. In general it is found that if the electrode under illumination is quite small with respect to the volume filled with metal vapor, or with respect to the surfaces present from which metal is evaporating, the effect of cooling the electrode is to condense fresh metal upon it in a finely divided highly sensitive form. If the temperature is then allowed to rise this fresh finely divided metal fuses together and becomes indistinguishable from metal condensed in the ordinary fashion at room temperature. If on the other hand the cooled surface is very large compared with the volume of vapor available the effects of condensation of vapor are comparatively small, and instead we have predominating the phenomenon originally found, namely the reduction of the photoelectric emission.

Without recording here the various experiments which support this explanation it is sufficient to state the experimental procedure to which these experiments lead, which in itself is excellent proof of the correctness of the explanation. This procedure consists in cooling the whole cell to a temperature far enough removed from the melting point of potassium to reduce its vapor pressure to negligible value, and using this temperature as the upper limit to the temperature changes impressed on the cell. This temperature, as is shown by experiments to be described elsewhere, on the effects of alkali metal vapors on thermionic emission, is about zero centigrade. Hence all that is necessary to entirely prevent the occurrence of the enhanced photoelectric emission on cooling these small central electrodes is to *pack the cell in melting ice;* a procedure used uniformly with this type of cell in the work which follows where the experiment under way required the cooling of the central electrode as the first step.

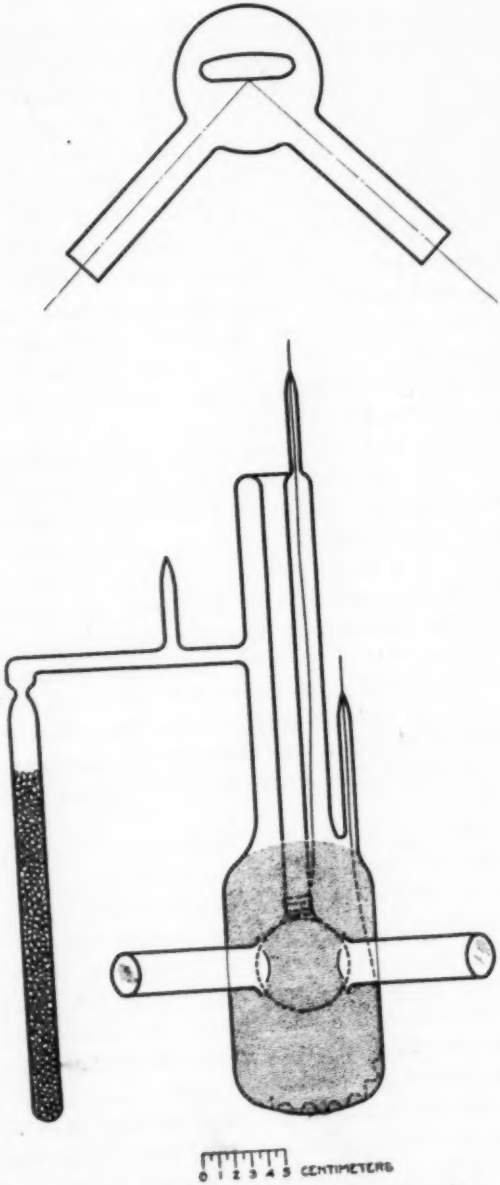


FIG. 7. *Cell with specular central electrode.*

As the outcome of the experience gained in these experiments, a special cell was designed intended to secure as near an approximation as possible to the conditions necessary for obtaining voltage-current curves of the type shown in Fig. 4. In this cell, shown in Fig. 7, the incident and reflected light beams pass through plane quartz windows fused on the ends of two tubes (stepped down from quartz to pyrex) standing at 90° to each other, and at 45° to the face of the central cathode. This cathode consists of a hollow tube with a flattened bulb at its lower end, one flat face of which is ground and polished optically flat. Potassium was first distilled into the cell and condensed on its walls and center, and then evaporated off the center by inserting an electric heating coil. Finally by gentle heating of a globule of potassium in one of the projecting tubes, a thin highly specular coating was distilled on to the flat cathode.

Two objects were aimed at in the production of this specular coating of potassium. The first was to minimize the scattering of any light upon the walls by having the light incident from one window reflected out through the other window of the cell. Only partial success was attained in this, as a slight reticulation of the mirror surface was sufficient to scatter enough light to the (rough and highly sensitive) walls to make the photoelectric emission from them still too large to permit measurements of stopping potentials. The second object was to permit measurements on the *normal* and *selective* photoelectric effects separately by the use of polarized light. Fair success was apparently attained in this, as the emission was considerably greater with the plane of polarization set for the selective than for the normal direction.

In certain other respects the cell fell considerably short of perfection; thus the cathode and anode were not so different in size as would have been desirable, so that saturation was not attained at zero field. Another defect due to the relatively large cathode was that the introduction of liquid air into it reduced the temperature of the cell walls near it; these latter should of course by preference be quite unaffected by any temperature changes of the cathode. In spite of these various shortcomings of this cell, however, results were obtained which are in entire accord with the hypothesis under study.

Fig. 8 shows the complete voltage-current relation, as obtained with yellow light, for the *selective* effect, at melting ice temperature and at liquid air temperature. The effect of liquid air is seen to be, in agreement with the preliminary results, a considerable reduction in the

saturation current. In the region below saturation the measurements actually show an increase of current. If, however, correction is made for the decreased emission from the walls, as shown by the lower arm of the curve, it is clear that the portion of the voltage-current curve below the new saturation value must be practically coincident with the original curve. A similar result is found with the *normal* effect, Fig. 9, in which, however, the effect of cooling is somewhat larger, a phenomenon which will probably ultimately be of some significance in the elucidation of the whole problem.

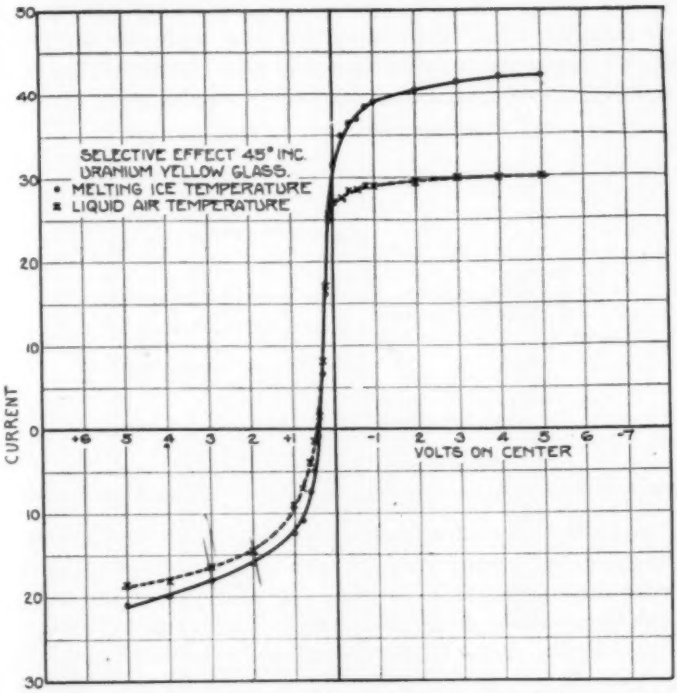


FIG. 8. *Voltage-current curves for the selective photoelectric effect, at 0° and −180° C.*

While, because of the difficulties of technique encountered, these results are not as clean cut as could be desired, they are entirely in accord with the hypothesis that the variation of photoelectric emission is due to a change in the work function acting in the manner pictured in Fig. 4.

## 5. CHANGE IN WORK FUNCTION ON COOLING DEMONSTRATED BY SHIFT OF THE VOLTAGE-PHOTOELECTRIC-CURRENT CURVE OF THE UNCOOLED ELECTRODE

It is now well established, from the work of Richardson and Compton,[9] Page,[10] and Millikan,[11] that a change in the material of the *cathode* does not alter the value of the stopping potential, or foot of the voltage-current curve. On the other hand, a change in the material of the *anode*, causes the whole voltage-current curve of the cathode emission to shift parallel to itself by the contact difference of potential (difference of work functions) between the original and the substituted anode material. This phenomenon has been made use of to furnish additional demonstration of the change in work function occurring when potassium is cooled from room to liquid air temperature.

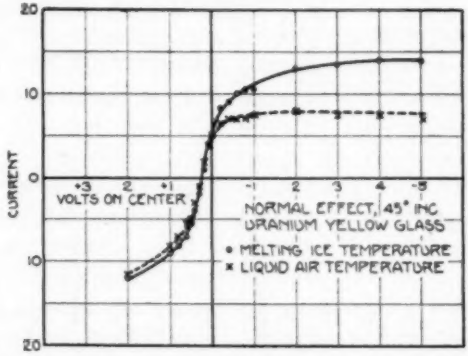


FIG. 9. *Voltage-current curves for the normal photoelectric effect, at 0° and −180° C.*

In contrast to the experiments described in the last section, the potassium to be cooled is now the *anode*, instead of the cathode. In order for the experiment to be clean cut this anode should be photoelectrically insensitive, so that the voltage current curve of the cathode alone may be observed. Practically this is not possible in a potassium filled tube. What one actually observes is the algebraic sum of the emission curves of the two electrodes, forming a double ended S shaped curve of the type shown in Fig. 6. What is wanted is some means for reducing to a minimum the emission (or more properly the observed current) from the electrode to be cooled so that any change in position of the part of the whole voltage-current curve contributed by the

[10] Page, Am. J. Sci., (4) *36*, p. 501; 1913.
[11] Millikan, Phys. Rev., *7*, p. 18; 1916.

uncooled electrode may show up clearly on the composite curve. It fortunately happens that a cell such as that shown in Fig. 10, con-

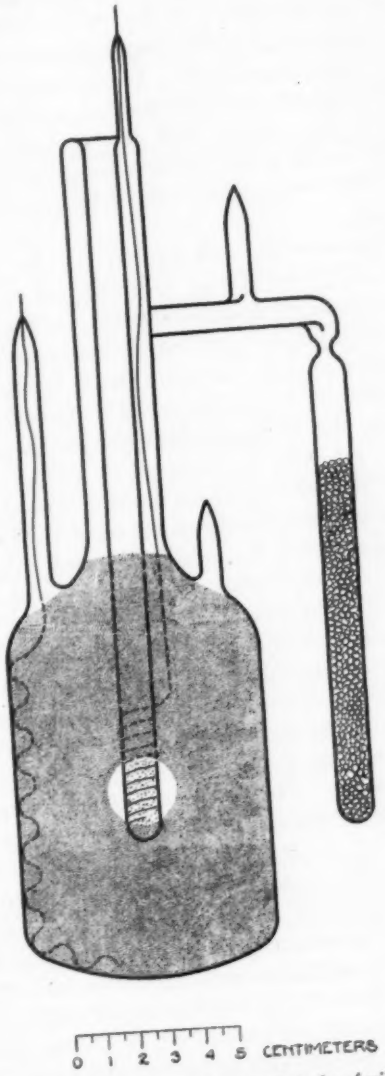


FIG. 10. *Cell with inner and outer potassium electrodes of widely different size.*

taining a hollow central electrode and walls completely coated with potassium naturally approximates to doing this, due to the much slower approach to saturation of the emission from the walls to the small center electrode, relative to that of the central electrode emission to the walls, a difference which becomes more marked the greater the ratio of area of the two surfaces. As a consequence the currents from the outer electrode are effectively multiplied by a progressively smaller factor the lower the voltage, with the net result that a considerable part of the shift in the emission curve from the inner electrode, caused by a change in the composition of the outer electrode, may be expected to remain visible.

The actual behavior to be expected from the type of cell just considered where the outer electrode is so changed that its work function is increased is illustrated diagrammatically by Fig. 11. In this figure the curves in the *A* region represent the emission from the center electrode considered alone, the curves in the *B* region, the emission from the outer electrode considered alone. The dashed lines designated by primed letters in the *B* region represent the behavior of the outer electrode alone, assuming its emission to become fully saturated at zero volts, while the full lines show the true type of curve due to poor saturation. We will imagine the whole cell first at room temperature; the voltage-current curves for the two electrodes separately are designated by $R_1$, the algebraic sum, or the curve which would be actually observed, by $M_1$. Let us now suppose that the work function of electrode *B* is increased, as is here supposed to be effected by cooling to the temperature of liquid air; the result will be, in accordance with our previous findings, a decrease in the emission from *B*, a shift of the saturation point to the right of the axis,—which will count for little because of the small size of the current there,—and a bodily shift of the emission curve from *A*. The new curves are shown by $L_1$, and the new mean by $M_2$. *There should accordingly occur a lateral shift of the mean curve.*

Let us now consider an additional experiment. With the cell in the condition just assumed, let us increase the work function of the inner electrode *A*, as by introducing liquid air. The emission from *A* will be decreased, and its saturation point moved to the left on the diagram, but the emission curve below the saturation point will probably be little affected. The emission curve from *B*, if it is saturated as shown by the dashed lines, will be shifted bodily to the left, as shown by $L_2'$; since, however, this shift is all to the right of the axis, where the true

current is quite small, its effect on the mean curve, whose region of interest lies almost wholly to the left of the axis, is negligible. Consequently the resultant mean curve $M_3$ is *unaltered as to the point at which it crosses the axis.*

In accordance with this analysis we should therefore anticipate the following behavior of a cell of the type described; when the exterior electrode is cooled the point of intersection of the voltage-current

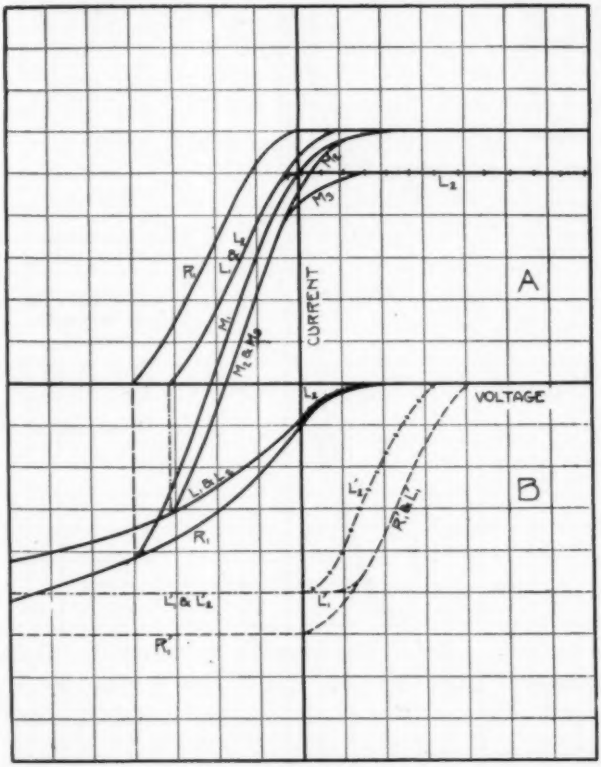


FIG. 11. *Diagrammatic representation of behavior of voltage-current curve of cell shown in Fig. 10 on cooling outer and inner electrodes.*

curve will shift along the axis; when the interior electrode is subsequently cooled, the point of intersection will remain unaltered.

This sequence of experiments is fortunately one in which, as above noted, the effects of metal vapor condensation are avoided, and so is

readily performed. The experiments, when made, entirely bore out the predictions of the above theory. In Fig. 12 are shown, by the full lines, the complete voltage-current curves of a cell of the type of Fig. 10

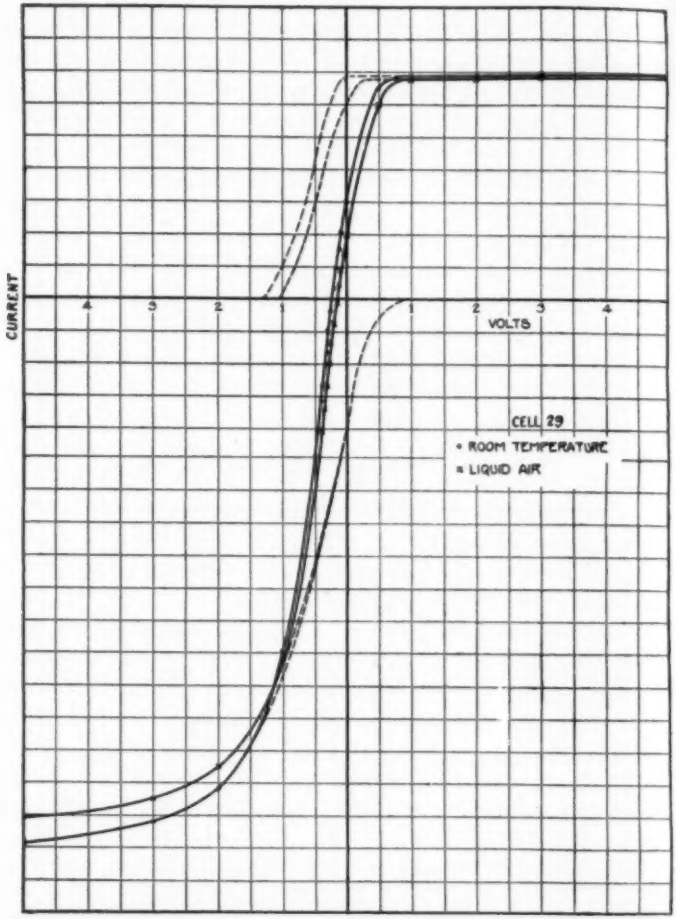


FIG. 12. *Voltage-current curves of cell shown in Fig. 10 at room and liquid air temperatures.*

with the external electrode first at room and then at liquid air temperature. The latter curve clearly exhibits the lateral shift of the sort predicted. The dotted curves, obtained by graphical extrapolation, indicate the probable positions of the voltage-current curves for each

electrode separately, under the two conditions. According to these curves the work function change in potassium in going from room temperature to liquid air temperature is approximately 1/5 of a volt.

In Fig. 13 are shown the data obtained upon carrying through the complete cycle suggested above, namely, placing the outer electrode in liquid air first and then later filling the inner electrode with liquid air. The result of the first experiment is to shift the voltage-current

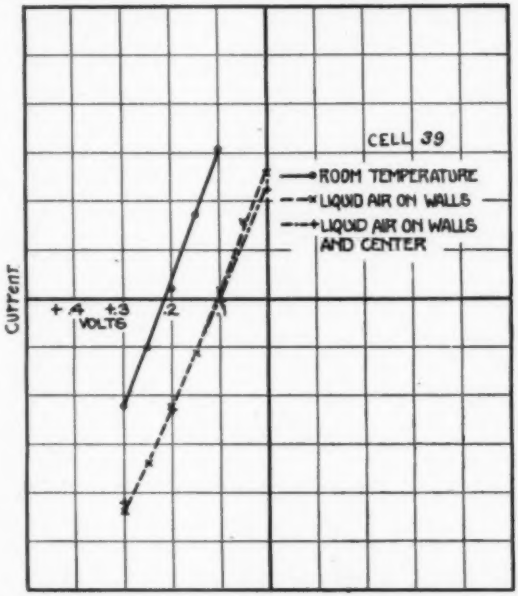


FIG. 13. *Effect of cooling outer and inner electrodes in succession.*

curve along the voltage axis as above described, while, after the second experiment, the curve is unchanged. These experiments appear to be very satisfactory proof of the theory tentatively adopted, that the effect of lowering the temperature of the potassium is to increase the work function of its surface.

Before concluding the discussion of this line of experiment attention may be called to a point of some interest. Considering the voltage-current curve of Fig. 12 below the axis as the emission curve of electrode *B*, it will be noticed that while the effect of the cooling process is to decrease the photoelectric current for the higher voltages, the result of the shift in the total curve is to make it appear that the electron

current from *B* to *A* is actually *increased* in the region of very low voltages. Turning back now to Fig. 2 it is seen that this effect was clearly exhibited in the preliminary experiments, made with cells in which the central electrode was a loop of thin wire; the explanation is obvious that the wire is photo-sensitive due to a coating of potassium and that the curves of Fig. 2 are each one arm of a complete S shaped curve such as those of Fig. 12.

### 6. Wave-length Distribution of Photoelectric Emission as Affected by Temperature; Long Wave Limit

The observations made with colored glasses as described in Section 2 suffice to establish the chief characteristics of the dependence of the temperature effect on wave-length. For the sake, however, of securing data which would be of the more strictly quantitative character desirable for theoretical discussion, the temperature effect was studied throughout the spectrum. For this purpose a cell of the type of Fig. 10 was used, taking the emission from the central electrode. For the first or high temperature curve, the whole cell was immersed and allowed to stand in liquid air in a Dewar flask with an illuminating window. The low temperature curve was then obtained by introducing liquid air into the central electrode. By this procedure, although the temperature range in the experiment was shortened by the general cooling of the whole cell by its immersion in liquid air, all danger was avoided of changing the medium through which the incident light reached the sensitive surface; at the same time, as above described, all the measurements were carried out below the temperature at which an appreciable quantity of potassium vapor was present.

The monochromatic light was obtained by means of a Hilger quartz monochromatic illuminator from a high efficiency tungsten filament operated at a temperature giving a visual match to a black body at 2848° absolute. The photoelectric current was measured by taking the potential drop by means of an electrometer across a high resistance in series with the cell and 300 volts battery. The results were reduced to terms of an equal energy spectrum from the known energy distribution of the source and the dispersion curve of the spectrometer.

The two curves so obtained are shown in Fig. 14. Confirming the earlier results with colored glasses, the effect of lowering temperature is to reduce the photoelectric current at all wave-lengths. The reduction is, however, proportionally much greater for the long wave-lengths. As can be seen on the curves there is no sharply defined long

wave-length limit,—the curves merely approach the axis asymptotically. This behavior is characteristic of all of the high vacuum cells containing highly purified potassium which have been measured. The only cases in which the long wave-length limit appeared sharply defined were in cells containing an appreciable amount of gas.

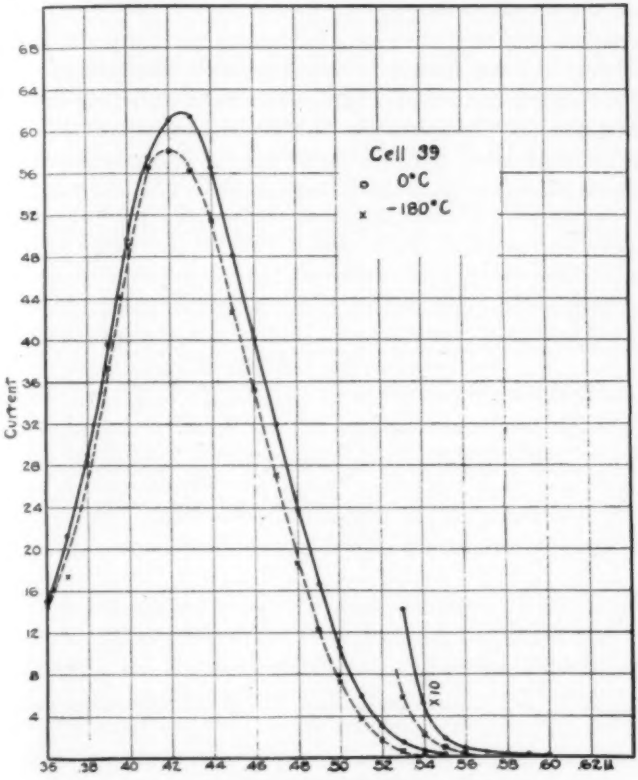


FIG. 14. *Distribution of response according to wave-length, room temperature and liquid air temperature.*

This absence of a well defined long wave-length limit prevents an accurate confirmation of the variation of work function by what should theoretically be one of the most elegant methods, that is, by the shift of the long wave-length limit. According to current photoelectric theory, the work function $w$ is equal to $h\,\nu_0$ where $\nu_0$ is the frequency corresponding to the long wave limit. Hence if the work function

changes from $w_0$ to $w_0'$, there should be a change in the long wave limit given by the equation:

$$\left(\frac{w_0 - w_0'}{h}\right) = \frac{e(V-V')}{h} = \nu_0 - \nu_0^1$$

or expressed in terms of $V-V'$, the change in contact potential difference, $V-V' = (h/e)\ (\nu_0 - \nu_0')$.

Bearing in mind that the long wave limit is not sharply defined, it is nevertheless of some interest to obtain precision measurements of the long wave end of the emission curves under the warm and cold conditions and get an approximate idea of what long wave limit shift may be reasonably interpreted from the data. Fig. 15 shows measurements of

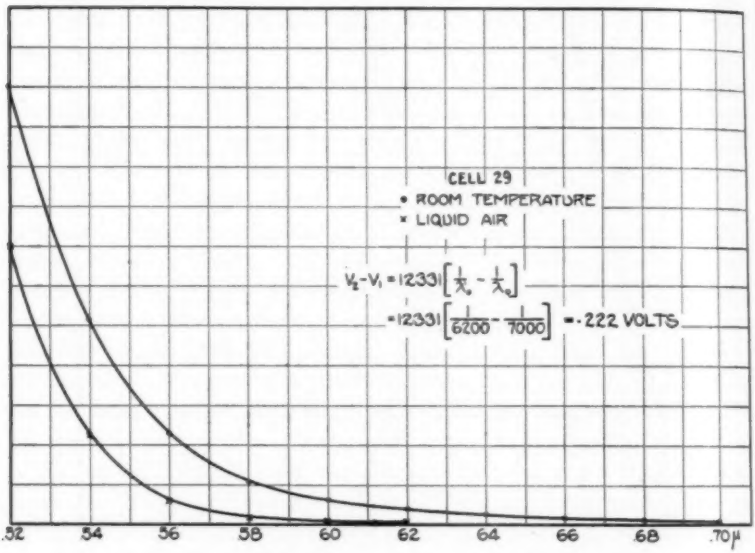


FIG. 15. *Emission in the long wave region of the spectrum, at room and liquid air temperatures.*

this sort made on the same cell as that used for the measurement of the shift in the voltage current curves (Fig. 12) and using the same (outside) electrode. By inspection of these curves, it was decided that the wave-lengths .62$\mu$ and .70$\mu$ probably represented the last points at which the true emission could with certainty be separated from the effects of scattered radiation and other sources of error. Introducing these two frequencies into the last equation with proper numerical

values of the constants we arrive at the value .22 for the corresponding change in contact potential difference. By comparing this with the variation deduced from Fig. 12, it is seen that the agreement as to order of magnitude of the change in work function with temperature is quite good.

## 9. DISCUSSION

Variations of the total photoelectric emission, and of the long wave limit, have been previously observed to occur with the age of the photo-sensitive surface, notably by Pohl and Pringsheim. The two kinds of variation with decrease of temperature which are here recorded, namely the increase due to condensation of metal vapor, and the decrease due to increase in the work function, differ from the changes previously observed, in their characteristic of easy reversibility. In all cases, however, it is probable that changes in total emission go hand in hand with changes in the long wave limit and the work function in the manner which has been demonstrated here for the case of the decrease of emission with lowered temperature.

There does not at the present time exist any theory of photoelectric emission which accounts for the exact shape of the distribution of emission according to wave-length and can prophesy in full what changes in this distribution should take place upon variation of the work function. The experimental data of this paper it is hoped will supply some of the information needed for the development of such a theory.

The nearest approach to a satisfactory theory of the photoelectric emission function is probably that given by O. W. Richardson,[8] and it has been found of considerable interest to compare the experimental results of this paper with such deductions as are possible from this theory. Richardson derives the following function for emission according to frequency:

$$F(\nu)=\frac{A_1 h}{R^2\nu^2}\left(1-\frac{w_0}{h\nu}\right)$$

This function bears little resemblance to the experimental curves. It does, however, call for a definite form of variation of the emission through the spectrum with change of the work function. Richardson's equation may be written the following way:

$$F(\nu)=\frac{A' h}{R^2\nu^3}(\nu-\nu_0)$$

If now we assume the work function to be changed from $w_0$ to $w_0'$ so that $\nu_0$ changes to $\nu_0'$, we can derive the following ratio for the emission at any frequency after and before the change

$$\frac{F'(\nu)}{F(\nu)} = \frac{\nu - \nu_0'}{\nu - \nu_0}$$

By inspection it will be seen that this calls for a ratio which increases with increasing wave-length as do the experimental curves derived in this study. Moreover it calls for just that "sliding" down of the saturation point along the straight line extending from $\frac{h}{e}(\nu - \nu_0)$, 0, to 0, $i_0$, in Fig. 4 which has been here assumed as the nature of the change introduced in the voltage current curve by change of $w$. In

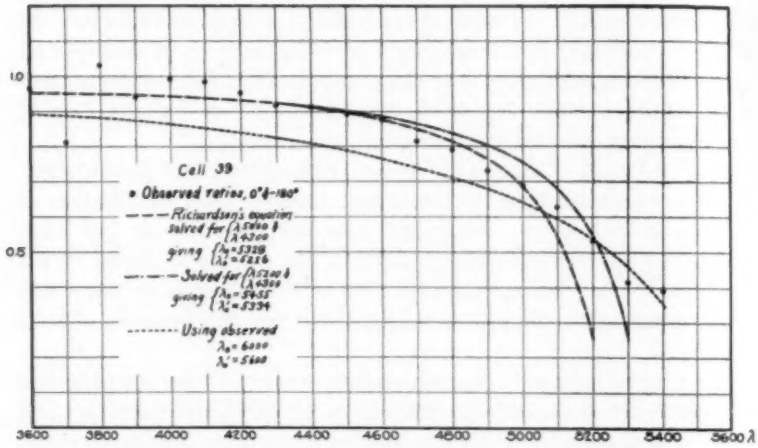


FIG. 16. *Observed and calculated ratios of emission through the spectrum at 0° and −180° C.*

order to see how accurately this relationship agrees with our experimental data, the curves of Fig. 16 have been calculated from the data of Fig. 14. Values for $v_0$ and $v_0'$ were first found by solving the equation just given through the use of experimental values at two wave-lengths; λ 5000 and λ 4300 were taken as one pair; λ 5200 and λ 4300 as another, and the ratios throughout the spectrum computed from the $\nu_0$ and $\nu_0'$ found. Next wave-lengths 6,000 and 5,600, which represent long wave limits which might without great forcing of the data be picked from the spectrum distribution curve, were used in a

similar manner. The circles represent the actual ratios from the curves of Fig. 14.

It will be seen from the curves of Fig. 16 that while the general trend of the ratios of "warm" and "cold" emission are given by the solution of Richardson's equation, the relationship is not in exact agreement with the data for any choice of the long wave limits. The data may be interpreted as calling for curves of varying convexity toward the origin of coordinates in Fig. 4, that is for curves more like the voltage current curves actually obtained by experiment. It is possible, however, that if all of the changes occurring in the material are taken into account, the relationship derived from Richardson's equation may not be greatly in error. In particular it is to be remembered that the potassium undergoes a change of possibly 10 percent in volume in going over the temperature range here considered. Lindemann[12] in his theory of the selective photoelectric effect develops a relationship $\lambda_{max} = \text{const } (\sqrt{a/n})$ where $a$ is the atomic volume. Accordingly as the atomic volume decreases the maximum of emission should move towards shorter wave-lengths. A bodily shift of the low temperature curve toward shorter wave-lengths will actually account for a large part of the discrepancy between the observed change in the emission curve and the prediction of Richardson's theory.

In ascribing the variation of photoelectric emission with temperature to a change in the work function of the emitting surface, the explanation of the phenomenon is of course only pushed back one stage further. It remains to be explained why the work function should change with temperature. Some consideration has been given to this question in the course of the present work, but without arriving at any definite result. One possibility considered was a change in the crystal structure of the potassium with change of temperature. This question was investigated by x-ray analyses by Dr. L. W. McKeehan,[13] who found that potassium at room temperatures is amorphous, but becomes definitely crystalline upon cooling toward liquid air temperature. On returning to room temperature the original amorphous state recurs. This behavior moves parallel to the photoelectric change with temperature. However, it appears that the crystal structure acquired by sodium at low temperatures persists when the temperature is raised again to room values. If there is a close connection between crystal structure changes and photoelectric emission we would expect with sodium to find the

[12] Lindemann, Verh. d. d. Phys. Ges., *13*, p. 482; 1911.
[13] McKeehan, Proc. Nat. Acad. Sci., *8*, p. 254; 1922.

reduction of photoelectric emission exhibiting a corresponding lack of reversibility. Experiment, however, showed that the photoelectric emission with sodium exhibits the same reversible characteristic with temperature change as that found with potassium. This appears to exclude the change of crystalline structure as the cause of the observed variation of work function.

Another possibility is that the metal surface is subjected to strain by the variation in volume of the metal under temperature change. The work function would thus be associated with the surface tension, a correlation which has been suggested by other work. The change in volume of the potassium over the temperature range in question is of the order of magnitude of 10 percent, which would be quite sufficient to introduce surface strains; perhaps, however, such a change in molecular spacing is in itself sufficient to cause a variation of the work function. In this connection a quotation from one of Richardson's papers[8] is of interest: "The variation of $w$ with $\theta$ is a matter of considerable practical interest. . . . From this rough view of the phenomena, one would expect that $w$ would diminish with rising temperature; its temperature coefficient being comparable with that of the linear expansion of the material."

RESEARCH LABORATORIES OF THE
AMERICAN TELEPHONE AND TELEGRAPH CO.,
AND THE WESTERN ELECTRIC COMPANY, INC.
JULY 24, 1923.

**Zeeman Effect of H-alpha and H-beta.**—Observations on the Zeeman effect of the first two lines of the Balmer series, looking perpendicularly to the magnetic field, with Lummer plates and echelons for the resolution. The components polarized parallel and normal to the field were separately photographed. The former (to accept the authors' convention in describing plane of polarization) which should occupy the positions of the components of the undisturbed lines, merge instead into a single line midway between them (at least at field strengths exceeding 10000 gauss). The result with H-beta eliminates the possibility present with H-alpha, that the strong line photographed is one of the components normally "prohibited" by the selection principle. The latter components, instead of being two doublets, form one doublet at the higher fields; apparently various stages of the transition from two doublets to one can be guessed at from the photographs, but they are difficult to interpret.—[K. Forsterling and G. Hansen, Jena; ZS. f. Phys. *18*, pp. 26–33; 1923.]

K. K. DARROW